

# Our Knowledge of the Atomic Constants $F$ , $N$ , $m$ , and $h$ in 1947, and of Other Constants Derivable Therefrom

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## I. INTRODUCTION

### A. Object and Scope

MANY critical reviews of the natural constants and conversion factors of physics have appeared in the last thirty years. The monumental work of R. T. Birge<sup>1</sup> in many papers published during this long period is outstanding in the field for its thoroughness and painstaking critical attention to every conceivable detail and to every source of information. Many other excellent studies have been made by a number of competent physicists dealing with this subject. There would be but little excuse for further contributions were it not for the fact that with the passage of time the situation becomes considerably modified (1) owing to new experiments and improvements in experimental techniques and (2) because of the broadening of our knowledge.

The present paper aims to deal only with a limited portion of the subject, the evaluation of the so-called atomic constants:  $e$  the electronic charge,  $m$  the electronic mass, and  $h$  Planck's constant of action together with certain auxiliary constants intimately associated with them. A number of useful physical constants which can be computed from the above data will also be evaluated.

The atomic constants  $e$ ,  $m$ , and  $h$  have been evaluated by means of many experiments which,

in general, measure *some function of one, two, or all three quantities, together with auxiliary constants*. In this process one obtains more equations than the number of unknowns and a certain amount of overdetermination thus results which permits us to discuss the *consistency* of the different determinations with each other. Over the long period during which the subject has been interesting to physicists this situation has led to a series of "discrepancies" each of a different nature, which, one after another, have been more or less resolved by further research and by improvements in the measuring techniques. Because of the entangled nature of the primary data each discrepancy, before its true cause had been located, appeared to offer a very complicated series of possibilities threatening extremely ramified modifications in the entire picture. Thus, for example, there was, at one time, much discussion of the " $e$  discrepancy." This appeared as a difference between the supposed "oil drop" value of  $e$  and the value computed from the Faraday  $F$  and Avogadro's number<sup>2</sup>  $N$  when the latter is determined by absolute length measurements of the atomic lattice dimension of crystals using x-ray wave-lengths standardized with ruled gratings. The discrepancy was resolved when the values originally used for the viscosity of air, in reducing the data from the oil drop experiment, were shown to be in error. Before this error was found, however, many other possibilities were explored and eliminated, some of which would have had very far reaching consequences if they had been true.

Another discrepancy which has occupied much attention and which is not yet completely resolved concerns the values of  $e/m$  as determined

<sup>1</sup> The authors are deeply indebted to Dr. Birge for help and criticism over a long period. They have relied extensively on his published work and his generous extensive private communications. A very abbreviated list of his more important published papers follows: R. T. Birge, *Rev. Mod. Phys.* **1**, 1 (1929); *Phys. Rev.* **40**, 207 (1932); *Phys. Rev.* **40**, 228 (1932); *Phys. Rev.* **42**, 736 (1932); *Nature* **133**, 648 (1934); *Nature* **134**, 771 (1934); *Phys. Rev.* **48**, 918 (1935); *Nature* **137**, 187 (1936); *Phys. Rev.* **54**, 972 (1938); *Am. Phys. Teacher* **7**, 351 (1939); *Phys. Rev.* **55**, 1119 (1939); *Phys. Rev.* **57**, 250 (1940); *Phys. Rev.* **58**, 658 (1940); *Phys. Rev.* **60**, 766 (1941); *Reports on Progress in Physics*, London, **VIII**, 90 (1942); *Am. J. Phys.* **13**, 63 (1945).

<sup>2</sup> We have endeavored to adhere as far as possible to the excellent nomenclature of Birge. Avogadro's number which Birge calls  $N_0$  we designate simply by  $N$  so that we can reserve the subscript zero to indicate what we call our conventional adopted origin values of the unknowns.

on the one hand by spectroscopic measurements and on the other hand by measurements involving deflections of electron beams by means of applied electric and magnetic fields.

Still a third discrepancy has lately attracted attention. This may be described by stating that the observed values of  $h/e$  (as measured by experiments on the quantum limit of the continuous x-ray spectrum) yielded significantly lower values than were obtained by computation from the best measured values of  $e$ ,  $e/m$ , and the Rydberg constant,  $R_\infty = 2\pi^2 me^4 h^{-3} c^{-1}$ . Both analytical and graphical examinations of the entire mass of data including the results of many other measured functions of  $e$ ,  $m$ , and  $h$  have led rather definitely to the conclusion<sup>3</sup> that the trouble lay with the measured x-ray values of  $h/e$ . These measurements have therefore recently been repeated by two different groups of workers<sup>4</sup> in the United States and in Sweden in quite different regions of the x-ray spectrum with most interesting results which not only indicate that this discrepancy has been practically eliminated but which also reveal the reasons for many of the earlier "low" experimental values of  $h/e$ . These new results open some new questions regarding minor corrections to the measured x-ray value of  $h/e$  which are unfortunately not yet completely resolved but which introduce, in the case of the American measurements, corrections only of the same order as the estimated probable error of the measurements themselves. They are, therefore, chiefly of theoretical interest at present. The situation regarding  $h/e$  is therefore far more satisfactory than it has ever been in the past for we are now in a position to reject, for good and sufficient reason, all earlier measured  $h/e$  values which were significantly "low," and we possess one measured  $h/e$  value which, as we shall show, can be justifiably incorporated along with nine other independent measured functions of  $e$ ,  $m$ , and  $h$  into a least squares solution

for the "best" values of those constants in the light of present knowledge.

This is one new element in the situation, the discussion of which is one of the justifications for the present paper. The other new element concerns a new viewpoint as regards the unknowns to be determined by least squares adjustment.

It must be admitted that the results still contain minor uncertainties which make it necessary to regard the present numerical values as provisional only. Further clarification of certain details in the  $h/e$  work with x-rays may a little later permit inclusion of the Uppsala values and may thus greatly improve the accuracy with which  $h/e$  is known. The situation regarding the  $e/m$  discrepancy may yet be still somewhat improved. The slight discrepancy between the iodine and silver values of the Faraday may be resolved in the future. To postpone the present paper until any or all such minor matters are cleared up would be unfortunate since it might involve a delay of several years. As E. U. Condon has pointed out, *there is a definite value in ascertaining and adopting generally acceptable standard values for the constants of physics at strategically chosen times, even though these values are admittedly provisional, since, by so doing, a desirable uniformity and consistency of usage in the literature is obtained.* In the judgment of the authors the present situation is sufficiently satisfactory to warrant such a provisional set of values and one of the purposes<sup>5</sup> of this paper is to present the evidence for this judgment.

It is this need for a standardized set of values, even though they be provisional, which is the only justification for the weighted averaging and least squares adjustments typical of the present paper. As H. A. Kramers has very aptly put it, "The theory of least squares is like love—one cross word can spoil it all." The procedure of

<sup>3</sup> F. G. Dunnington, Rev. Mod. Phys. **11**, 65 (1939); J. W. M. DuMond, Phys. Rev. **56**, 153 (1939) and Phys. Rev. **58**, 457 (1940); F. Kirchner, Ergebnisse der Exakten Naturwiss. **18**, 26 (1939).

<sup>4</sup> W. K. H. Panofsky, A. E. S. Green, and J. W. M. DuMond, Phys. Rev. **62**, 214 (1942); Per Ohlin, Dissertation, Uppsala (1941); Arkiv. f. Mat. Astr. och Fysik **27B**, No. 10; **29A**, No. 3; **29B**, No. 4; **31A**, No. 9; **33A**, No. 23.

<sup>5</sup> In 1940 a continuing committee of the National Research Council known as the "Committee on Fundamental Constants and Conversion Factors" was formed under the chairmanship of Dr. L. J. Briggs as a joint committee under the N. R. C. Divisions of Chemistry and Physics with the stated purpose of ascertaining and publishing from time to time the best and most generally acceptable values of the physical constants. Responsibility for the subdivision of the atomic constants was assigned to one of the authors of the present paper and its contents therefore constitute a report to the above mentioned committee.

TABLE IA. Experimental sources of information in determining  $e$ ,  $m$ , and  $h$ . "Old" or traditional viewpoint.

Description of experiment	Quantity determined	Numerical value	Function of $e$ , $m$ , and $h$ determined	Auxiliary constants involved
1. Spectroscopic determinations of the Rydberg wave number equated to Bohr's formula.	$A_1 = 2\pi^2 me^4 h^{-3} c^{-1} = R_\infty$	$R_\infty = 109737.3$	$me^4 h^{-3}$	$c$
2. Direct determinations of $e$ by the ruled grating and crystal x-ray method.	$A_2 = e = F/N$	$e = 4.80193 \times 10^{-10}$	$e$	$F; N$ $N = M_{\text{CaCO}_3} [2d^3 \rho \varphi(\beta)]^{-1}$
3. Specific charge of the electron (spectroscopic methods, deflection methods or other).	$A_3 = e/m$	$e/m = 1.75903 \times 10^9$	$em^{-1}$	$F; \phi; q; c$
4. Measurements of the quantum limit of the continuous x-ray spectrum.	$A_4 = h/e$	$h/e = 1.3786 \times 10^{-17}$	$he^{-1}$	$\phi; q; c; \lambda_0/\lambda_S$
5. Electron diffraction measurements of DeBroglie wave-lengths for electrons accelerated with a measured voltage.	$A_5 = h/(em)^{\frac{1}{2}}$	$h/(em)^{\frac{1}{2}} = 1.00084 \times 10^{-8}$	$he^{-\frac{1}{2}} m^{-\frac{1}{2}}$	$\phi; q; \lambda_0/\lambda_S$
6. X-ray photoelectrons ejected with known quantum energies, $h\nu$ , and measured by magnetic deflection.	$A_6 = e^2/(mh)$	$e^2/(mh) = 3.8197 \times 10^{34}$	$em^{-\frac{1}{2}} h^{-\frac{1}{2}}$	$\lambda_0/\lambda_S; c$
7. Determinations of fine structure constant $\alpha$ .	$A_7 = 2\pi e^2/(hc) = \alpha$	$\alpha = (136.95)^{-1}$	$e^2/h$	
8. DeBroglie wave-length by electron diffraction in which the speed of the electrons is measured kinematically. Compton shift measurements.	$A_8 = h/m$	$h/m = 7.267$	$h/m$	$\lambda_0/\lambda_S$
	$A_{8c} = h/m = c\lambda_0$	$h/m = 7.255$	$h/m$	$\lambda_0/\lambda_S; c$

obtaining adjusted values by weighted averages of many different experiments (whose disagreements are most probably in part the result of unknown systematic errors) has been severely criticized in many quarters. The school of thought which opposes such a procedure has no better alternative to offer, however, than to

TABLE IB. Directly observed values of auxiliary constants.

	Source*
Velocity of light $c = (2.99776 \pm 0.00004) \times 10^{10}$ cm sec. <sup>-1</sup>	Birge
Avogadro's number** $N = (6.02338 \pm 0.00043) \times 10^{23}$ mol <sup>-1</sup> (chemical scale)	Birge
Atomic weight of calcite $M_{\text{CaCO}_3} = 100.091 \pm 0.005$ (chemical scale)	Birge
Density of calcite $\rho = 2.71029 \pm 0.00003$ g cm <sup>-3</sup>	Birge
Calcite volume factor $\varphi(\beta) = 1.09594 \pm 0.00001$	Birge
Conversion from Siegbahn to absolute wave-lengths $\lambda_0/\lambda_S = 1.002030 \pm 0.000020$	Birge
Grating space of calcite $d_{20} = (3.03567 \pm 0.00005) \times 10^{-8}$ cm	Birge
Faraday** $F = 9648.5 \pm 1.0$ e.m.u. equiv. <sup>-1</sup> (chemical scale)	Recalculated
Conversion from NBS international electrical units to absolute units	
1 NBS ohm = $p$ absolute ohm $p = 1.000495$	NBS
1 NBS volt = $pq$ absolute volt $pq = 1.000330$	NBS
1 NBS ampere = $q$ absolute ampere $q = 0.999835$	NBS
Atomic weights (physical scale)	
H $1.008131 \pm 0.000003$	Mattauch
D $2.014725 \pm 0.000006$	Mattauch
He $4.003860 \pm 0.000031$	Mattauch
Gas constant per mole. $R_0 = (8.31436 \pm 0.00038) \times 10^7$ erg mol <sup>-1</sup> deg. <sup>-1</sup>	Birge
Volume of perfect gas (0°C) $V_0 = (22.4146 \pm 0.0006) \times 10^3$ cm <sup>3</sup> atmos. mol <sup>-1</sup>	Birge

\* Birge: R. T. Birge, *Reports on Progress in Physics* (1941), Physical Society, London (1942). NBS: National Bureau of Standards, private communication (see text). Mattauch: J. Mattauch, *Nuclear Physics Tables* (Interscience Publishers, Inc., New York, 1946).

\*\* The values of the Faraday and Avogadro's number given here are the *observed* values and *not* the least square adjusted values of Table VIII. The latter are to be considered as the "best values." See Birge, *Am. J. Phys.* 13, 63 (1945).

wait hopefully for still better experimental results and, in the meanwhile, to be completely noncommittal as to adoption of values. The practical result of this, however, is a woeful lack of uniformity in the literature since writers are continually obliged to make calculations involving the constants.

There is really no danger in the use of statistical theory for the calculation of adjusted values of the physical constants with their resulting probable errors, *provided we do not forget the provisional character of the results*. If unknown systematic errors are present in the original data, we can only hope that, with a sufficient number of independent experiments, even the systematic errors will tend to have a random distribution. Since we *must* determine provisional values from a supply of partially inconsistent data, *the most convenient tool we have is a least squares adjustment*. It furnishes an impartial analytic method of determining a set of compromise values which do the least possible violence to all our sources of information.

## B. The Experimental Sources of Information

The experiments which yielded the data used in the present paper have usually been classified into eight types, each of which determines a different function of the variables  $e$ ,  $m$ ,  $h$ . In Table IA we list these in the order of decreasing precision and reliability giving, the function determined, a description of the (one or more)

experiments which determine it, and the numerical value  $A_i$  at present adopted for each function together with its probable error as estimated from the determining experiment or experiments. Certain auxiliary constants are also needed in each determination and these are also listed in the formulae, Table IA. Their definitions and adopted values are given in Table IB. In the computation of some of the derived constants at the end of this paper a few additional auxiliary constants are needed and these, for completeness, are also listed in Table IB. In succeeding sections we shall discuss the sources of all these data and our reasons for the adopted values and precision measures.

### C. The Entangled Nature of the Data

R. T. Birge has justly pointed out that in the analysis of data such as we must deal with here it is extremely important (1) to distinguish the primary data of experiment from derived data and (2) to ascertain clearly just what function of the unknowns each experimentally determined numeric really stands for. Constants such as  $R_\infty$  or  $c$  whose relative error is very small in comparison to the majority of the unknowns

can, of course, be treated as accurately determined numbers. This is not true, however, of all the auxiliary constants and, as we shall presently see, the Faraday  $F$  and Avogadro's number  $N$  are particularly important cases of primary data which should be allowed independent freedom of adjustment in a least squares compromise solution. In the past it has been customary to introduce the quotient  $F/N=e$ , the electronic charge, as a single primary datum. However,  $F$  and  $N$  appear separately and in different ways in the formulae for the determination of constants other than  $e$  that form, in some instances, part of our primary data and, in other cases, data to be derived. Therefore, the only strictly logical procedure is to treat  $F$  and  $N$  as independent unknowns. The electronic charge  $e$  then has the status of a derived constant. Although both  $F$  and  $N$  have each been determined by experiment, there is no guarantee that the adjusted values of these constants resulting from a least squares compromise solution of the overdetermined set of equations in which they are involved will be exactly equal to the original directly observed experimental values of  $F$  and  $N$ .

The adoption of this new viewpoint constitutes the second important new element in the

TABLE II. Experimental sources of information in determining  $F$ ,  $N$ ,  $m$ , and  $h$ . New viewpoint.

Description of experiment	Quantity determined	Numerical value	Function of $F$ , $N$ , $m$ , and $h$ determined	Auxiliary constants involved
1. Spectroscopic determinations of Rydberg wave number equated to Bohr's formula.	$A_1 = 2\pi^2 me^4 h^{-3} c^{-1} = R_\infty$	$R_\infty = 109737.3$	$F^4 N^{-4} m h^{-3}$	$c$
2. Direct determinations of Avogadro's number by ruled grating and crystal x-ray method.	$A_2 = M_{\text{CaCO}_3} [2d^3 \rho \varphi(\beta)]^{-1} = N$	$N = 6.02338 \times 10^{23}$	$N$	$M_{\text{CaCO}_3}$ , $d$ , $\rho$ , $\varphi(\beta)$
3. Direct determinations of the Faraday (silver and iodine voltameters).	$A_3 = F$	$F = 9648.5$	$F$	$p$ , $q$
4. Atomic weight of the electron by spectroscopy.	$A_4 = mN$	$Nm = 5.48541 \times 10^{-4}$	$Nm$	
5. Specific charge of the electron by deflection methods and Zeeman effect.	$A_5 = e/m$	$e/m = 1.75920 \times 10^9$	$FN^{-1} m^{-1}$	$p$ , $q$ ; $c$
6. $F(e/m)$ from Bearden's x-ray refractive index of diamond.	$A_6 = F(e/m)$	$F(e/m) = 1.69870 \times 10^{11}$	$F^2 N^{-1} m^{-1}$	$p$ , $q$ ; $c$
7. Measurements of quantum limit of continuous x-ray spectrum.	$A_7 = h/c$	$h/c = 1.3786 \times 10^{-17}$	$F^{-1} N h$	$p$ , $q$ ; $c$ , $\lambda_a/\lambda_S$
8. Electron diffraction measurements of DeBroglie wave-lengths for electrons accelerated with a measured voltage.	$A_8 = h/(em)^{\frac{1}{2}}$	$h/(em)^{\frac{1}{2}} = 1.00084 \times 10^{-8}$	$F^{-\frac{1}{2}} N^{\frac{1}{2}} m^{-\frac{1}{2}} h$	$p$ , $q$ ; $\lambda_a/\lambda_S$
9. X-ray photoelectrons ejected with known quantum energies, $h\nu$ , and measured by magnetic deflection.	$A_9 = e^2/(mh)$	$e^2/(mh) = 3.8197 \times 10^{84}$	$F^2 N^{-2} m^{-1} h^{-1}$	$\lambda_a/\lambda_S$ , $c$
10. Determinations of fine structure constant $\alpha$ .	$A_{10} = 2\pi e^2/(hc) = \alpha$	$\alpha = (136.95)^{-1}$	$F^2 N^{-2} h^{-1}$	
11. DeBroglie wave-length by electron diffraction in which the speed of the electron is measured kinematically. Compton shift measurements.	$A_{11} = h/m$ $A_{11c} = h/m = c\lambda_c$	$h/m = 7.267$ $h/m = 7.255$	$m^{-1} h$ $m^{-1} h$	$\lambda_a/\lambda_S$ $\lambda_a/\lambda_S$ ; $c$

present analysis. It leads to the adoption of Table II for the description of our primary sources of information. Under the new viewpoint the chief changes are three in number:

(1) *Two* unknowns,  $F$  and  $N$ , are introduced in place of the one unknown,  $e$ .

(2) Three quite different and independent types of experiment, all of which have in the past traditionally been regarded as determining  $e/m$ , on the new viewpoint now fall into three separate classes: (a) spectroscopic experiments (such as those on the  $H$  and  $D$  lines) *which really determine the atomic mass of the electron*; (b) "deflection" experiments which are legitimate determinations of  $e/m$ ; and (c) Bearden's measurement of the refractive index of diamond for x-rays which really measures the product  $F(e/m)$ .

(3) The ruled grating and crystal x-ray determinations traditionally regarded as determinations of  $e$  are now classified as what they really are, direct determinations of Avogadro's number  $N$ .

In the application of the new viewpoint the auxiliary constants used are still those of Table IB. We must however distinguish the directly observed  $F$  and  $N$  of that table from the final adjusted values of these constants which we shall receive as the result of all least squares adjustments. (Actually it turns out that  $N$  suffers very little change from the directly observed value, but this could hardly have been predicted.)

Because this new viewpoint represents a considerable break with tradition, we have thought it wise to work the entire problem through by *both* methods so that the results can be compared. We shall distinguish the two methods merely by the adjectives "old" or "traditional" on the one hand and the adjective "new" on the other hand. We believe the results by the new method are those that should be recommended for temporary adoption simply because they do less violence to *all* of the known data with appropriate weighting.

It should be pointed out that it is the wholehearted espousal of the principle of least squares adjustment in the present work which forces us to the adoption of the new viewpoint. In the past the usual procedure was to apply the prin-

ciple of least squares merely to finding the best representative value of each directly measured quantity (a weighted average value of  $R_\infty$ , for example, or a weighted average value of  $F$ ). Then a definite *path* was selected for computing each derived constant *utilizing the most accurate primary data* as the criterion for selection of the path. This path was as follows: combining  $F$  and  $N$  one obtained  $e$ . Then combining  $e = F/N$  with the best adjusted mean value of  $e/m$  and with  $R_\infty = 2\pi^2 me^4 h^{-3} c^{-1}$  one solved the three equations for  $e$ ,  $m$ , and  $h$ . In computing other derived constants one took pains always to express them in terms of the primary data ( $e/m$ ,  $R_\infty$ ,  $e$ ). Other paths for arriving at the results could conceivably have been used (taking an example at random) such as to combine  $e = F/N$  with the observed value of  $\alpha = 2\pi e^2 h^{-1} c^{-1}$  and  $R_\infty = 2\pi^2 me^4 h^{-3} c^{-1}$  to solve for  $e$ ,  $m$ , and  $h$ . Such a possible path was not used for the obvious reason that it was much less accurate because of the relatively large uncertainty in the determination of  $\alpha$ . A simple enumeration shows that even if  $R_\infty$  is always included as one of the data, there are still some 15 different paths by which one could evaluate the atomic constants. To select the most accurate path, however, amounts to attaching zero weight to a great deal of information and the present situation as regards consistency seems sufficiently satisfactory (as we shall endeavor to show below) to warrant a more inclusive procedure.

When we make a least squares adjustment of *all* the data, however, we have abandoned the choice of any specific path. We must first decide what we shall consider as fixed constants and what shall be regarded as unknowns. Let  $U$  be the number of unknowns. Then we write down all equations in which experimentally determined functions of these constants and unknowns are equated to the numerical values which the experiments yielded. The number of these equations,  $E$ , considerably exceeds the number  $U$  of unknowns and the equations are not exactly compatible, but the theory of least squares teaches a definite procedure for finding compromise values of the unknowns which do the least possible violence to each of the determinations, taking due account of the relative weights which we attribute to each equation in

view of its estimated probable error. The final adjusted values of the unknowns will differ slightly from those arrived at by any particular path in which some selected set consisting of only  $U$  of the total of  $E$  equations was used.

Our least squares adjustment procedure under the old viewpoint is to select as unknowns  $e(=F/N)$ ,  $m$ , and  $h$  and to classify  $F$  and  $N$  among the fixed constants. The application of the principle of least squares then to the nine<sup>6</sup> equations represented in column 2 of Table IA leads us to adjusted values of  $e$ ,  $m$ , and  $h$ . *But the adjusted value of  $e$  turns out to be not quite equal to the quotient of the constants  $F$  and  $N$  initially inserted.* If we indicate final adjusted values by bold faced type, the results are as follows:<sup>7</sup>

Inserted value

$$F = 9648.5 \pm 1.0 \text{ e.m.u. (chemical scale).}$$

Inserted value

$$N = (6.02338 \pm 0.00043) \times 10^{23};$$

$$cF/N = e = (4.80193 \pm 0.0006) \times 10^{-10} \text{ e.s.u.}$$

Adjusted value

$$c\mathbf{F}/\mathbf{N} = \mathbf{e} = (4.80214 \pm 0.00047) \times 10^{-10} \text{ e.s.u.}$$

<sup>6</sup> Equation (1) for  $R_\infty$  is so accurate (i.e., deserves so much weight) that it can merely be used to eliminate one of the unknowns from all the others before applying the principle of least squares. Equations (7), (8), and (8c) all essentially determine  $h/m$  since  $c$  is known with sufficient accuracy to regard it as a fixed constant. There are therefore really six independent equations for the adjustment of two unknowns.

<sup>7</sup> Throughout this paper we indicate the accuracy with which a quantity is known by quoting the figure  $0.6745\sigma$ . The standard deviation,  $\sigma$ , of the mean of  $N$  weighted observations is given by

$$\sigma^2 = \sum p_i v_i^2 / (N-1) \sum p_i$$

where  $p_i$  are the weights assigned to each observation and  $v_i$  are the deviations of each observation from the weighted mean of the set. The range of the number such that the probability is 0.5 that the correct value lies within that range is called the probable error ( $PE$ ). It is well known that for observations that have a Gaussian distribution about the mean value,  $PE = 0.6745\sigma$ . In the general theory of the least squares fitting of several variables, the standard deviation of each variable can be defined in a definite manner which involves only the observed quantities and is independent of any detailed assumptions as to the nature of the distribution from which the data were taken. The probable error on the other hand is more difficult to determine and requires a knowledge or at least an assumption of the form of the distribution functions. However, since the quantity usually used by physicists is the probable error, we have defined, somewhat loosely and arbitrarily, the probable error to be  $PE = 0.6745\sigma$  and quote this value although the standard deviation  $\sigma$  is the quantity which actually results from our analysis.

*The question then immediately arises as to what we shall call our separate adjusted values of  $\mathbf{F}$  and  $\mathbf{N}$  since the adjustment under the old viewpoint has only given us an adjusted value for their ratio.* The conclusion that our adjustment under the old viewpoint did not provide a sufficient number of degrees of freedom is thus forced home. It becomes even more acutely evident when we must compute derived constants from our adjusted values of  $e$ ,  $m$ , and  $h$ . Many of these involve  $F$  and  $N$  not only implicitly in the variable  $e$  but also explicitly in such a way that they cannot be expressed as functions of  $F/N$  alone. To be consistent we must decide on separate adjusted values  $\mathbf{F}$  and  $\mathbf{N}$  to use in the computation of these derived constants. Therefore, in our procedure under the old viewpoint we have adopted the quite arbitrary method of determining  $\mathbf{F}$  and  $\mathbf{N}$  by adjusting the relative deviations  $|\mathbf{F}-F|/F$  and  $|\mathbf{N}-N|/N$  so as to make these directly proportional to the squares of the probable errors (inversely proportional to the weights) of the *direct determinations* of  $F$  and  $N$ , respectively, while imposing the further condition that  $\mathbf{F}/\mathbf{N}$  shall equal our adjusted value of  $e$ . By so doing we have departed from the thoroughgoing application of the least squares principle because, for example, some of our other determinations, notably those usually classified as determinations of  $e/m$ , contain implicit information regarding  $F$  to which some weight should be attached. This is why we cannot recommend the old viewpoint values.

To summarize we may say that the old viewpoint assumes three unknowns, say  $e$ ,  $m$ , and  $h$ , which number can be reduced to two by the application of the Rydberg relation, while the new viewpoint assumes four unknowns  $F$ ,  $N$ ,  $m$ , and  $h$  equivalent to three after application of the Rydberg relation. The larger number of variables under the new method introduces an unavoidable difficulty in depicting the situation graphically.

#### D. Graphical Representations to Depict the Interconsistency of the Data

In the analysis of such complicated situations as the present one, graphical aids are of great utility in forming judgments even though they may not be used to obtain numerical results. In

this connection the Birge-Bond diagram, as it is called, has rendered very valuable service. To construct such a diagram one particular unknown, such as  $e$ , is selected for plotting. R. T. Birge has described in detail the construction of such diagrams, and the reader is referred to his 1932 article for the description. Birge more recently plots scales on the ordinates which read directly in terms of the function to which each corresponds. In the latest diagram of this type<sup>8</sup> Birge selected the two ordinates representing (1) the "direct" determination of  $e$  (from  $F$  and the x-ray determination of  $N$ ), and (2) the best average of all  $e/m$  determinations (some of which involve  $F$  and some of which do not) as the determining ordinates for drawing his straight line. He states that a least squares adjustment would lead to substantially the same results as this line yields. The data then available, especially when represented in this way, certainly did not seem to warrant such an adjustment because of the  $h/e$  discrepancy and the rather weak weights that would have been attached to all data save  $e$  and  $e/m$  on his chart.

For our present discussion we prefer to utilize a different kind of graphical representation developed some years ago by one of us<sup>9</sup> because it lends itself somewhat more readily to the kind of thinking which our present method of least squares adjustments requires. This graph which was originally called an "Isometric Consistency Chart" was designed from the old viewpoint regarding  $e$ ,  $m$ , and  $h$  as the unknowns and we shall explain it in these terms. We wish it clearly understood that this chart has never been and is not now intended as a nomogram for arriving at adjusted best values. It is merely a way of depicting the interconsistency of input data with each other and with the adjusted value arrived at by least squares computations. It also offers a convenient method of exhibiting the "ellipse of error."

Consider a three-dimensional space in which the values of the three unknowns  $e$ ,  $m$ , and  $h$

appear plotted on mutually rectangular cartesian coordinate axes. To each point in the space there corresponds a triplet of values,  $e$ ,  $m$ ,  $h$ . Each equation of column 2, Table IA, defines a surface in this space. These surfaces all very nearly pass through a common point. In this region of quasi-intersection a slight change in the experimentally determined constants  $A_i$  of these equations will displace the corresponding surface in the direction of its normal. It turns out that the relative changes in the  $A$ 's needed to bring all surfaces into coincidence at a single point are all less than 0.5 percent and indeed most are of order 0.1 percent. Only negligible second-order errors, therefore, are introduced if we replace the surfaces (which are, in general, curved) by planes tangent to these surfaces in the region in question. It then becomes our object to study these variously tilted planes in the region where they nearly intersect in a common point. We can think of the least squares solution as an analytic method of selecting a point in this space in such a way that the sum of the weighted squares of its relative distances from all of the planes shall be minimized. The weights, according to the theory of least squares, are to be adjusted so as to be inversely proportional to the squares of the estimated probable errors of each determined  $A_i$ . The thought behind this procedure is, of course, that each such weighted plane represents a small sample out of a much larger universe of observations which, if they had all been made, would have yielded Gaussian distributions for the positions of all planes whose centers would all have passed consistently through a common point of the space. This is an assumption, nothing more, but in the absence of better information it is about the best we can do. A further consequence of this assumption is that there exists in this space an "ellipsoid of error" defined by the different Gaussian distributions of the planes. We shall discuss this a little later.

It is desirable to eliminate dimensional considerations from our problem and therefore our procedure is to select an origin point  $e_0$ ,  $m_0$ ,  $h_0$  in the  $e$ ,  $m$ ,  $h$  space whose relative distance from each of the planes shall be small and to define new dimensionless variables  $x_e = (e - e_0)/e_0$ ,  $x_m = (m - m_0)/m_0$ ,  $x_h = (h - h_0)/h_0$ , the relative de-

<sup>8</sup> See R. T. Birge, "The general physical constants as of August 1941 with details on the velocity of light only," Reports on Progress in Physics 8, 124 (1942). For a description of the construction of the Birge-Bond diagram see R. T. Birge, Phys. Rev. 40, 228 (1932) and, in particular, pages 232-5 and 252.

<sup>9</sup> J. W. M. DuMond, Phys. Rev. 56, 153 (1939); 58, 457 (1940).

viations of our original unknowns from the arbitrary origin values, all of which, it turns out, are a small fraction of one percent. In terms of these new variables each of our experimental equations of type

$$e^i m^j h^k = A_{ijk}$$

becomes a linear equation of type

$$ix_e + jx_m + kx_h \cong a_{ijk}, \quad (1)$$

wherein each  $a$  is defined as  $a = (A - A_0)/A_0$ . Here  $A_0$  is the origin value of  $A$ , that is to say,

$$A_0 = e_0^i m_0^j h_0^k. \quad (2)$$

The approximate Eq. (1), which is the equation of the tangent plane to each observed surface in our space of relative deviation from the arbitrary origin, neglects second-order terms in the binomial expansions which are of order one part per million since the variables are of order 0.1 percent. Our problem is thus linearized, and we now have a set of eight different linear equations of the type of (1) in three unknowns which are not exactly compatible and which are to be adjusted by the standard procedure of least squares. These equations take the following form:

	Relative Weights	
$4x_e + x_m - 3x_h = a_1$	$\infty$	
$x_e = a_2$	65	
$x_e - x_m = a_3$	13	
$-x_e + x_h = a_4$	12	
$-\frac{1}{2}x_e - \frac{1}{2}x_m + x_h = a_5$	3	(3)
$2x_e - x_m - x_h = a_6$	0.9	
$2x_e - x_h = a_7$	7.3	
$x_m - x_h = a_8$	(8) 0.7; (8c) 0.1.	

The subscripts of the  $a$ 's correspond to the numbering in column 2 of Table IA. The first of the above eight equations which corresponds to the Rydberg relationship must be given so much more weight than any of the others because of its high accuracy that, in practice, the best procedure is to eliminate one of the variables from the entire set by means of it *before* proceeding to the least squares adjustment.

At this point let us examine how our eight tangent planes *look* in the  $x_e, x_m, x_h$  space. First let us consider only their orientations. For this purpose we can set the  $a$ 's all equal to zero since this merely shifts each plane in the direction of

its normal. The coefficients of the variables in the eight equations (3) above form a matrix characterized by certain properties which are invariant to any transformation of axes and are, therefore, of fundamental importance in understanding the situation. From this matrix of eight rows and three columns, fifty-six different third-order determinants can be formed and *twelve of these determinants vanish*. Geometrically, each of these means that the corresponding set of three planes contains a common axis in the space. Such a set of three planes constitutes a degenerate case which defines a line but which is incapable of locating a point in the space. If the  $a$ 's are not zero this means for such a degenerate case that the three planes are parallel to a common line, though they may not pass through it. Now it turns out that, out of our present set of eight planes, *actually five of them are parallel to a common line*. These are the ones numbered 3, 4, 5, 6, and 8. This line makes equal angles with the three axes  $x_e, x_m, x_h$ . The matrix defines only two other axes to which more than two planes are parallel, but neither of them is associated with as many planes as this one.<sup>10</sup> Adopting a term from crystal structure we shall speak of planes which are parallel to a common axis as belonging to a "zone" and such a set of planes will be described as a "cozonal" set. If we think of the positive octant of our  $x_e, x_m, x_h$  space, then the five planes are parallel to and very nearly contain a line through the origin making equal acute angles with the three positive axes. If we look at the planes along this direction, we shall see all five of them on edge. There remain only three planes, (1) the  $R_\infty$  plane, (2) the  $e$  plane, and (7) the  $e^2/h$  plane determined by the value of the fine structure constant  $\alpha$ . The last of these is considerably less accurately known than the first two. One way of stating the situation, then, is that five of our eight equations are only capable of defining *ratios* between the constants  $e, m$ , and  $h$ . This drives home forcefully the extreme responsibility of the first two of our equations in determining the three unknown constants  $e, m$ , and  $h$ . Once the position in space of a best fitting cozonal axis has been established

<sup>10</sup> A complete enumeration of all such axes is given in a previous paper, J. W. M. DuMond, Phys. Rev. **58**, 459 (1940), see Fig. 1.



for the five cozonal planes, the remaining two planes may or may not intersect this axis in the same point.<sup>11</sup> In this respect the overdetermination is evidently not as high as it could have been in the case of a less degenerate matrix. It is, therefore, very fortunate that the two planes in question happen to represent the two most accurate determinations of all.

Because of this particular degenerate peculiarity of the set the isometric consistency chart was constructed as a view projected on the (111) plane of the  $x_e, x_m, x_h$  space of the five cozonal planes (seen on edge) which therefore appear as lines on the chart. Each line is provided with its own scales, normal thereto, giving displacements of that line corresponding to different positive or negative percent deviations of the function in question from the origin value of that function. In order to represent on the two-dimensional diagram the non-cozonal planes (2) and (7), recourse is had to the Rydberg relation which is considered to be essentially exact. Geometrically, this amounts to finding the lines of intersection of planes (2) and (7) with the Rydberg plane and *projecting each of these lines in space on the (111) plane of our isometric chart.* (The reason for the name "isometric" is now obvious. It is borrowed from drafting terminology.) Any axis determined by the cozonal planes will be seen end-on and will appear as a point on this chart. If either the plane (2) (direct determination of  $e$ ) or the plane (7) (determination of  $\alpha$ ) cuts this axis at the same point as the  $R_\infty$  plane (1), then the projected intersection line for that non-cozonal plane will, on our chart, pass through the point. Scales are also provided to show displacements of the non-cozonal lines calibrated in percent deviation of the corresponding functions from their origin values. It is furthermore easy in the same way to provide displacement scales for lines corresponding to *any* function of the three variables  $e, m, h$  whether they belong to the isometric zone or not and, in particular, it is convenient to provide scales for  $m$  and  $h$  on the chart. To every point on the chart, therefore, there corresponds a value of  $e, m$ , and  $h$  whose percentage deviation from the origin values  $e_0, m_0, h_0$  can be read off di-

rectly on the appropriate scales. To distinguish scales for the non-cozonal variables from the rest, *two* lines are drawn along the lengths of these while one line only is drawn along the divisions for cozonal scales.

Figure 1 shows on our isometric consistency chart the experimental data of Table IA. The least squares adjustment of these data yields the point indicated by a small white circle at the center of the black ellipse. This point shows graphically the best adjusted values of  $e, m, h$  and functions thereof *under the old viewpoint* according to which these three are regarded as the primary unknowns. These results *which we do not recommend* together with a few of the derived constants are listed numerically later in this article for comparison with our recommended values.

Examination of this chart permits us to form a judgment regarding (1) the general consistency of the input data, (2) their estimated (input) probable errors (which are represented by two lines equally and appropriately spaced on either side of the center line for each variable), (3) the deviation of each input datum from the adjusted best value, and (4) the probable errors of the adjusted best values of  $e, m$ , and  $h$  and functions thereof. The probable error of the adjusted best value of  $e, m, h$  or any function thereof is given by the width of the black error ellipse *projected on the scale for the variable or function whose probable error is desired.* In order to exhibit this situation more clearly we show in Fig. 2 this error ellipse to much larger scale than in Fig. 1. The probable error spread of each variable or function is emphasized with a heavy black stroke along the corresponding scale. This brings us quite naturally to a discussion of the determination of the precision measures for the adjusted values of variables and functions thereof resulting from such a least squares adjustment as ours.

### E. The Problem of Estimating Precision Measures

Probably the most important new concept which is introduced regarding the calculation of precision measures from a least squares adjustment such as the present one is that of the existence of correlation coefficients. We are accus-

<sup>11</sup> The spacial appearance has been shown in a perspective view, Phys. Rev. 56, 156 (1939), Figs. 1 and 2.

to the well-known "propagation of errors" formulae for computing the probable error in a function of certain variables for each of which a probable error is given.<sup>12</sup> What is less obvious and much less generally understood is that such straightforward application of the principle of propagation of errors *leads to correct results if*

*and only if the input variables are strictly independent (uncorrelated).*

Consider the case of two independent variables,  $x$  and  $y$  which have standard deviations  $\sigma_x$  and  $\sigma_y$ , illustrated in Fig. 3. In accord with the hypothesis of the theory of least squares we assume that many observations of these vari-

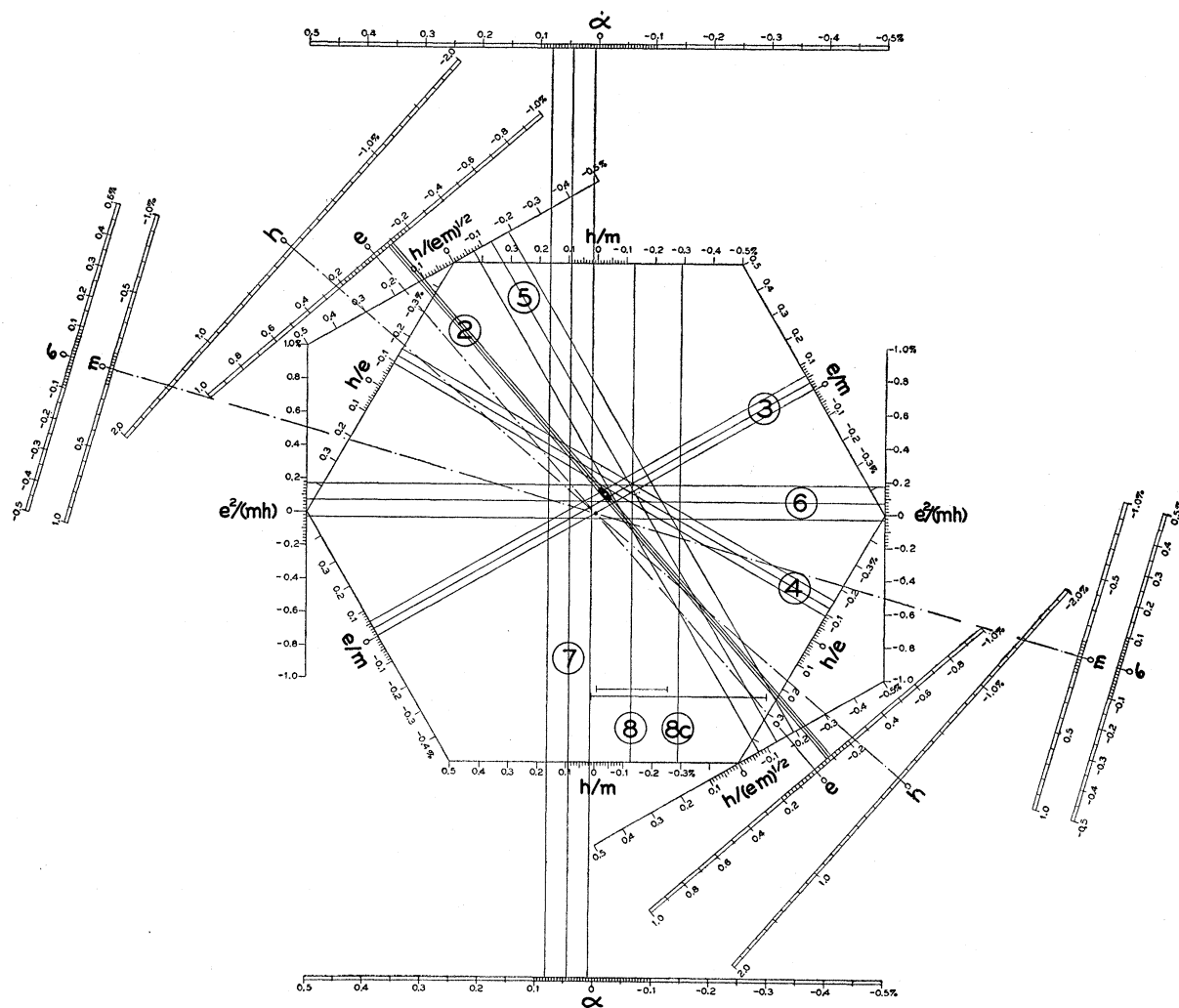


FIG. 1. Isometric consistency chart showing the experimental input data (Table IA) and the least squares adjusted best value *under the old viewpoint*. The adjusted values are given by the white circle in the center of the small black ellipse which latter is the ellipse of probable error. We do not recommend this least squares adjustment under the old viewpoint, and this chart is shown only for comparison with the results obtained under the new viewpoint (see Figs. 9 and 10). The axes of  $e$ ,  $m$ , and  $h$  are shown with dot and dash lines. The origin values are given in Section III-A. This cut has not been revised to accord with certain small corrections to our numerical values found necessary after the paper had been submitted. Such changes are wholly unimportant.

<sup>12</sup> We use the expression "correlation coefficient" for lack of a better word. The quantities  $F$ ,  $N$ ,  $m$ , and  $h$  are not correlated in the strict statistical sense but are *observationally related* since we do not observe each one independently of the others. The numbers expressing this relationship are mathematically the same as correlation coefficients as defined, for example, in Kenney, *Mathematics of Statistics* (D. Van Nostrand Co., Inc., New York, 1939), Vol. II, Chap. VI. For a discussion of the Law of Propagation of Errors, see R. T. Birge, *Am. Phys. Teacher* **7**, 351 (1939).

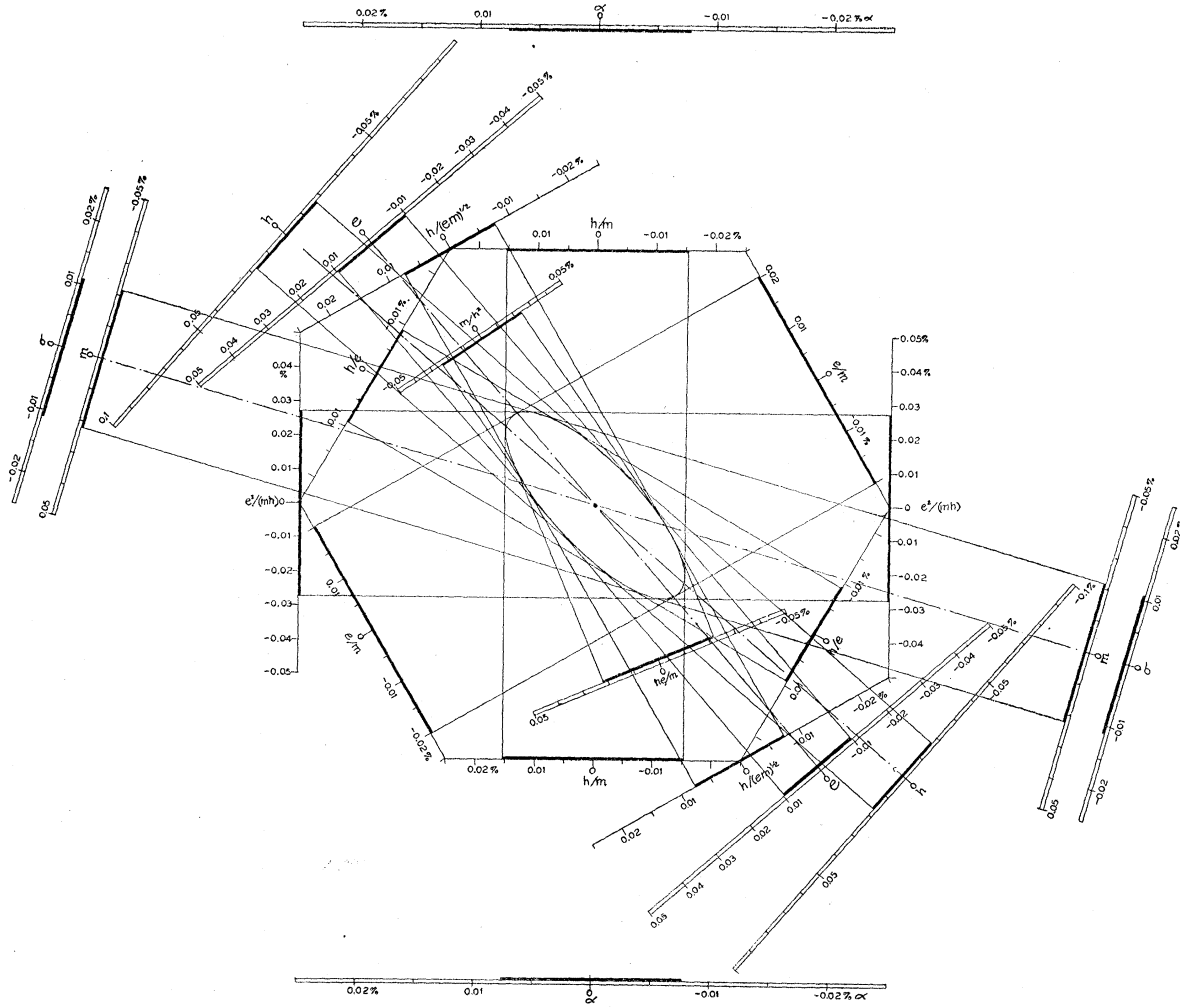


FIG. 2. The probable error ellipse to large scale. The projected width of the ellipse on the scales for the different variables and functions gives the (marginal) probable error spread for each in percent (old viewpoint).

ables would lead to different observed values which would occur with Gaussian frequency distributions about a mean value  $\mathbf{x}$  and  $\mathbf{y}$ . These frequency distributions are indicated with shading in Fig. 3. When we say that the variables are independent or uncorrelated, we mean that the method used for measuring the variables was such that the chance of observing a particular value  $x_1$  in the small range  $dx$  is completely independent of any observation which may have been made regarding  $y$  and, conversely, for  $y$  regarding  $x$ . Thus the chance of observing  $x$  at the value  $x_1$  in the range  $dx$  and simultaneously observing  $y$  at the value  $y_1$  in the range  $dy$ , that is to say, the chance that the observations will

fall in the small black area of the graph, is simply the product of the independent chances. Analytically we can write

$$\begin{aligned} & \text{(for any value of } y) P(x-\mathbf{x})dx \\ &= (2\pi)^{-\frac{1}{2}} \sigma_x^{-1} \exp[-(x-\mathbf{x})^2/(2\sigma_x^2)]dx, \quad (4) \end{aligned}$$

$$\begin{aligned} & \text{(for any value of } x) P(y-\mathbf{y})dy \\ &= (2\pi)^{-\frac{1}{2}} \sigma_y^{-1} \exp[-(y-\mathbf{y})^2/(2\sigma_y^2)]dy, \quad (5) \end{aligned}$$

and thus

$$P(x-\mathbf{x}, y-\mathbf{y})dxdy = (2\pi\sigma_x\sigma_y)^{-1} \exp[-(x-\mathbf{x})^2/(2\sigma_x^2) + (y-\mathbf{y})^2/(2\sigma_y^2)]dxdy. \quad (6)$$

Clearly, the lines of constant probability form a

system of similar ellipses in the  $x, y$  space with major and minor axes parallel to the axes of  $x$  and  $y$ . We can think of a "probability hill," as it is frequently called, having elliptical contours for its horizontal sections and Gaussian distribution curves for all its vertical sections. The particular ellipse plotted in Fig. 3 is then the ellipse of standard deviation. An ellipse of probable error (of dimensions 0.6745 times the one shown) would contain within it just half the volume of the hill.

Now let us consider certain variables *derived* from  $x$  and  $y$ , say  $u = x + y$  and  $v = x - y$ . In Fig. 4 the axes of these variables, which make angles of  $45^\circ$  with those of  $x$  and  $y$ , are shown, together with the original ellipse of standard deviation for observations of  $x$  and  $y$ . In the  $u, v$  coordinates, however, the principal axes of the ellipse are oblique. This implies the existence of correlation coefficients for  $u$  and  $v$ . At a specified value of  $u$ , say  $u_1$ , the Gaussian cross section of the probability hill along the line  $AA$  has its maximum at  $M$  and with variation of  $u_1$  this maximum point follows along the oblique locus  $RR$ . This line passes through the horizontal tangent points of the ellipse because the ellipse is one of the level contours of the hill. Such a locus is called a regression line. Clearly then, for any specified value of  $u$  the most probable value of  $v$  varies with  $u$ , and this is what is meant by saying that  $u$  and  $v$  are correlated. If we make no specification regarding  $u$ , then the projected shape of the hill on the  $v$  axis gives the probability distribution which describes our knowledge of  $v$ . This is called the marginal probability distribution for  $v$ . It can be readily shown that the projected widths of the oblique ellipse of standard deviation on the  $u$  and  $v$  axes give the respective (marginal) standard deviations  $\sigma_u$  and  $\sigma_v$  for these variables in the way indicated in Fig. 4 by the horizontal and vertical tangents to the ellipse. It is not difficult to show that these standard deviations can be computed from the standard deviations for  $x$  and  $y$  by the simple application of the law of propagation of errors but this is only true because  $x$  and  $y$  are uncorrelated. This gives us

$$\sigma_u = (\sigma_x^2 + \sigma_y^2)^{\frac{1}{2}} \quad \text{and} \quad \sigma_v = (\sigma_x^2 + \sigma_y^2)^{\frac{1}{2}}. \quad (7)$$

Since  $u$  and  $v$  are correlated variables we cannot

compute the standard deviations of functions of  $u$  and  $v$  by simple application of the laws of error propagation. As a trivial example to drive this fact home, let us compute the standard deviation in the functions  $\xi = (u+v)/2$  and  $\eta = (u-v)/2$ . The law of error propagation gives:

$$\sigma_\xi = \sigma_\eta = \frac{1}{2}(\sigma_u^2 + \sigma_v^2)^{\frac{1}{2}}. \quad (8)$$

If (8) were correct, substituting (7) into it we should have

$$\sigma_\xi = \sigma_\eta = \frac{1}{2}\sqrt{2}(\sigma_x^2 + \sigma_y^2)^{\frac{1}{2}}. \quad (9)$$

But actually  $\xi$  and  $\eta$  are nothing but  $x$  and  $y$  and have, therefore, standard deviations  $\sigma_\xi = \sigma_x$  and  $\sigma_\eta = \sigma_y$  so that we see that the ordinary application of the propagation of errors to the correlated variables  $u$  and  $v$  has led to incorrect results.

R. T. Birge, in his evaluations of the constants, has been generally careful to avoid the above difficulty by expressing all of his formulae for derived constants directly in terms of his primary observed data which are uncorrelated in most cases because the measurements were independent in nature.<sup>13</sup>

When we pass to the case of a least squares adjustment such as we make in the present

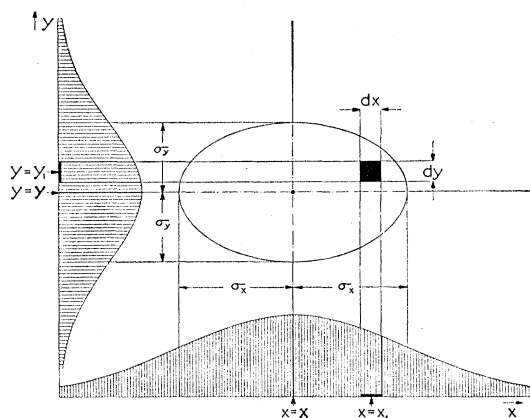


FIG. 3. Illustrating the two-dimensional elliptical Gaussian error distribution function for two independently observed variables,  $x$  and  $y$ , having standard deviations  $\sigma_x$  and  $\sigma_y$ , respectively. The ellipse of standard deviation is shown. It is one of the contours of the error distribution.

<sup>13</sup> An outstanding exception to this, however, is the case of  $e$  and  $e/m$  which he treats as primary data but which are correlated because some of the spectroscopic determinations which contribute to the weighted average value of  $e/m$  involved  $F$ , as did also  $e$ . Our present computations under the old viewpoint are subject to the same objection.

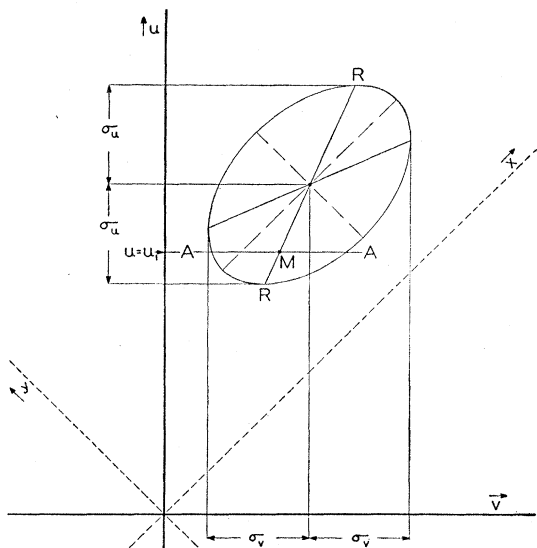


FIG. 4. The ellipse of standard deviation for two variables derived from  $x$  and  $y$  of Fig. 3, namely,  $u=x+y$  and  $v=x-y$ . In contrast to  $x$  and  $y$  which were independently observed,  $u$  and  $v$  are correlated in the observational sense.

paper, all variables must be regarded as having correlation coefficients. We make the assumption that there exists in the space of our primary variables an ellipsoid of error whose principal axes will lie, in general, oblique to the axes of any of the variables or their functions. Our limited number of weighted observations of the different variables and their functions lead us by standard least squares procedures to a putative ellipsoid which most nearly expresses the deviations of our data from exact precision and consistency. This is the higher dimensional analog of fitting a Gaussian distribution in one variable to a limited number of observations of that variable.

Suppose that by independent direct observations on two variables  $x$  and  $y$  we have found them to have the values  $x=1.00\pm0.10$  and  $y=0.80\pm0.07$  and that we have also, by a third independent direct observation, found that  $u=x+2y=3.00\pm0.07$ . These three observations are not rigorously consistent. This situation is graphed in Fig. 5; the three heavy lines representing the input observations do not intersect in a common point. Their input probable error bands are shown with dashed lines. This situation is expressed by the following set of observa-

tional equations:

	Weight $p_i$ :
$x=1.00\pm0.10$	1,
$y=0.80\pm0.07$	2,
$x+2y=3.00\pm0.07$	2,

the weights being adjusted inversely as the squares of the input probable errors. The standard procedure of least squares leads to the normal equations for the adjusted values:

$$\begin{aligned} 3x + 4y &= 7.0, \\ 4x + 10y &= 13.6, \end{aligned}$$

with the solution

$$x=1.1143, \quad y=0.9143,$$

with standard deviations

$$\sigma_x=0.1807, \quad \sigma_y=0.0990,$$

and with the correlation coefficient

$$r=-0.7303.$$

The equation of the error ellipse (for standard deviation) is

$$\begin{aligned} 1 &= [\sigma_y^2 x^2 - 2r\sigma_x\sigma_y xy + \sigma_x^2 y^2] / \sigma_x^2 \sigma_y^2 (1-r^2) \\ &= [3x^2 + 8xy + 10y^2] / 0.045715. \end{aligned}$$

The best or adjusted output values  $x$  and  $y$  are the coordinates of the dot in Fig. 5 surrounded by the ellipse of error (standard deviation). The standard deviation in each of the output values is given by the projected width of the ellipse. *Since this ellipse need not necessarily have its principal axes parallel to any of the input variables, it is not safe to compute standard deviations or probable errors as though any of these variables were uncorrelated.*

Since the procedure for computing errors in the case of statistically correlated variables is well known,<sup>14</sup> it will not be explained here. All our probable errors have been computed by these standard methods which give the marginal probable errors and the correlation coefficients for the different variables and their functions. In a three-dimensional space this amounts geometrically to finding the half-spread between the

<sup>14</sup> A good account of the entire procedure which we have found very useful is given in a recent paper, Henri Mineur, "Extension de la méthode des moindres Carrés, application à la détermination de l'apex au moyen des mouvements propres," Ann. d'Astrophysique 7, 121 (1944).

two parallel tangent planes to the error ellipsoid, the planes being those associated with constant value of the particular variable or function considered. In the space of  $x_e$ ,  $x_m$ , and  $x_h$  the precision of the Rydberg relation makes the error ellipsoid *negligibly thin in the direction normal to the Rydberg plane*, i.e., the ellipsoid flattens out into a two-dimensional ellipse described on that plane. This is the ellipse which (projected on the isometric plane) appears in Figs 1 and 2. Its size and orientation are consequences of the probable errors (i.e., weights) assigned to the input data and of the mutual incompatibilities of the observational Eqs. (3).

Examination of Fig. 1 shows that even on the old viewpoint our input data do not deviate badly from the adjusted best values, if these deviations are compared with the estimated input probable errors. These input probable errors were estimated entirely from considerations internal to the experiment which yielded each one without any *a priori* consideration of consistency on the chart. The situation is at least as good as this and possibly a little better under the new viewpoint, although it is not possible to exhibit it quite so clearly because of the addition of an extra variable.

Because of the greater familiarity which readers may have with the isometric chart for the variables  $e$ ,  $m$ ,  $h$  and also because of the greater interest which centers in these variables, we have confined ourselves in this paper to exhibiting the results of our least squares adjustment under the new viewpoint (independent variables  $F$ ,  $N$ ,  $m$ , and  $h$ ) by means of the old  $e$ ,  $m$ ,  $h$  chart. Our  $e$ ,  $m$ ,  $h$  space is now, however, in reality only one cross section of a four-dimensional  $F$ ,  $N$ ,  $m$ ,  $h$  space. The particular cross section we show is the one for which  $N$  is constant at its adjusted best value. The chart, therefore, fails to show the consistency picture in its entirety. These results are shown later in this article in Fig. 9 and the resulting probability ellipse is given in Fig. 10 to an enlarged scale.

It will be noted in Fig. 9 that, under the new viewpoint, four very good independent determinations agree quite satisfactorily so that their input probable error intervals overlap the adjusted best value and the remaining determina-

tions do not deviate badly when their input probable errors are taken into consideration. Figure 10 shows us that the ellipse of probable error under the new viewpoint is much more nearly circular (less correlation) than under the old viewpoint and also somewhat smaller.

## II. SELECTION OF THE PRIMARY INPUT DATA

The task of selection of reliable data for our computation is greatly lightened by the numerous excellent studies of R. T. Birge, J. A. Bearden, F. G. Dunnington, members of the staff of the National Bureau of Standards, and others which have here been freely used as indicated by our references.

### A. $R_\infty$ , the Rydberg Wave Number for a Nucleus of Infinite Mass

In an important recent study<sup>15</sup> carried out with meticulous attention to every detail and many experimental sources, R. T. Birge arrives at the final best value which he recommends for adoption:

$$R_\infty = 109737.303 \pm 0.017 \text{ cm}^{-1} \text{ (I.A. scale)} \\ \text{or } \pm 0.05 \text{ cm}^{-1} \text{ (c.g.s. scale).}$$

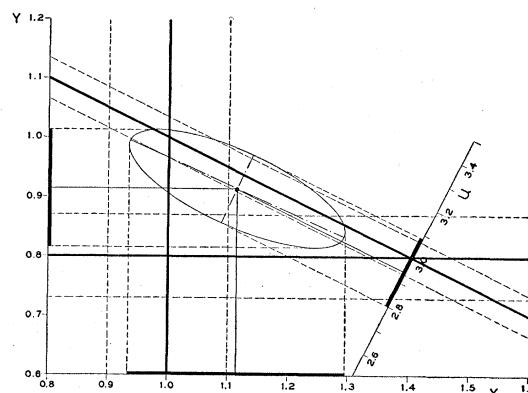


FIG. 5. To illustrate the case of an overdetermined set of data. Here two variables  $x$  and  $y$  are directly observed and also a function of these variables  $u = x + 2y$  has been directly observed. The input data, represented by the three heavy black lines, are not exactly interconsistent since they do not intersect in a common point. The input probable errors are shown with dashed lines equally spaced on either side of each heavy line. The best or adjusted values of  $x$  and  $y$  are given by the coordinates of the dot at the center of the ellipse of standard deviation. The output standard deviations associated with the adjusted best value are shown as the projected widths of the ellipse on the scales for  $x$ ,  $y$ , and  $u$ .

<sup>15</sup> R. T. Birge, "The values of  $R$  and of  $e/m$  from the spectra of H, D, and He<sup>+</sup>," Phys. Rev. 60, 766 (1941).

This important datum is considerably more accurately known than our present calculations require. Therefore, we have rounded it off to

$$R_{\infty} = 109737.3 \text{ cm}^{-1}$$

and have treated it as an exactly known constant.

### B. The Electrical Conversion Factors from International to Absolute Units

As a result of a long series of researches<sup>16</sup> carried out in different national standards laboratories of the world the following revised conversion factors<sup>17</sup> have been decided upon for official adoption as of January 1, 1948.

For the ohm:

(One mean N. B. S. International ohm =  $p$  absolute ohms)

$$p = 1.000495.$$

For the volt:

(One mean N. B. S. International volt =  $pq$  absolute volts)

$$pq = 1.00033.$$

For the ampere:

(One mean N. B. S. International ampere =  $q$  absolute amperes)

$$q = 0.999835.$$

In our calculations we have adopted the above values.

### C. The Faraday Constant, $F$

The Faraday has been determined with precision by two different methods, the silver voltameter and the iodine voltameter.<sup>18</sup> Unfortunately, the results disagree by an amount considerably in excess of the estimated probable errors of either method. R. T. Birge<sup>19</sup> has dis-

cussed this matter in his 1941 review of the general physical constants and has arrived at a weighted average compromise value based on considerations as to the possible systematic errors in the two determinations. As one of us has pointed out in private correspondence with Dr. Birge, the silver determinations were all made before the discovery of isotopes and since natural silver consists of two isotopes,  $\text{Ag}^{107}$  and  $\text{Ag}^{109}$ , in nearly equal abundance, we have the best possible situation favoring a change in the average atomic weight of the electrodeposited silver through selective deposition. (Natural iodine, on the other hand, is a pure substance,  $\text{I}^{127}$ .) A rough calculation based on the assumption that the ratio of the abundance ratios (before and after deposition) may be equal to the ratio of the square roots of the two masses shows that this source of error alone could account for a large part of the Ag-I discrepancy. Unfortunately, to close up the gap, the silver value of  $F$  must be *raised* but if the selective deposition is accounted for simply by the difference in ion mobilities in the solution it is the *lighter* isotope which one would expect to deposit more rapidly so that the sign of the shift would be in the wrong sense. However, selective electrolytic separation of isotopes is a complicated affair and nothing is known in this connection regarding silver. *For this reason the authors feel that a complete revision of the whole situation regarding the experimental determination of the Faraday in the light of our modern knowledge is urgently needed.*

A summary of absolute measurements of the value of the Faraday made in three countries between 1910 and 1931 is given in a paper<sup>20</sup> presented at the Congres International d'Electricité, Paris, 1932 by G. W. Vinal of the (American) National Bureau of Standards. G. W. Vinal and L. H. Brickwedde in a private communication, prepared for the N. R. C. committee on constants at the request of one of us, sums up the entire situation and arrives at a value which when corrected for the new value of  $q$  yields:

$$F = 9648.5 \pm 1.0 \text{ absolute e.m.u. per equivalent} \\ (\text{chemical scale of atomic weights}).$$

<sup>16</sup> For a complete summary see H. L. Curtis, N. B. S. Research paper, RP1606 from Bur. Stand. J. Research **33**, 235 (1944).

<sup>17</sup> Communicated to the authors in a letter dated May 12, 1947, from E. C. Crittenden, Associate Director, National Bureau of Standards.

<sup>18</sup> E. W. Washburn and S. J. Bates, J. Am. Chem. Soc. **34**, 1341, 1515 (1912). G. W. Vinal and S. J. Bates, Bull. Bur. Stand. **10**, 425 (1914).

<sup>19</sup> R. T. Birge, "The general physical constants," Reports on Progress in Physics **8**, 112, 115 (1942). See also R. T. Birge, Am. J. Phys. **13**, 63 (1945).

<sup>20</sup> G. W. Vinal, "Le voltametre à argent," Comptes rendus, Congres International d'Electricité, Paris, **3**, 95 (1932).

Vinal and Brickwedde assigned a probable error of  $\pm 0.6$  but in view of the uncertainties we have increased this to accord with R. T. Birge's estimated probable error. This is the value which we shall adopt in the present paper. In arriving at this value Vinal and Brickwedde weighted the silver and the iodine results equally. Birge's 1941 value of the Faraday differs only insignificantly from this.

#### D. The Avogadro Number, $N$

By far the most accurate and reliable values of the Avogadro number  $N$  are obtained by utilizing x-ray wave-lengths, calibrated in absolute units by very accurate measurements with ruled gratings at grazing incidence, to determine the absolute dimensions of the unit cells of crystals such as calcite. From the density of the calcite and the absolute volume of this unit cell the absolute molecular weight in grams can be calculated and this combined with the chemical atomic weight yields Avogadro's number. Before the oil-drop value of  $e$  had been corrected by revisions regarding the true viscosity of air, the above method of arriving at  $N$  was questioned since it led to a value of  $e$  (in the neighborhood of  $4.80 \times 10^{-10}$  e.s.u.) then supposed to be too high. This was a fortunate thing since it led to a great deal of very careful and critical examination<sup>21</sup> of all possible sources of error, both theoretical and experimental, in the above (x-ray) method of arriving at  $N$ . The method has successfully withstood this criticism and is now generally believed to be thoroughly reliable. An excellent summary of the entire experimental situation as regards  $N$  by the x-ray method has been given by J. A. Bearden<sup>22</sup> and in a still more recent paper by R. T. Birge<sup>22</sup> in which the work over a considerable period of time of four entirely independent experimenters, Bearden, Bäcklin, Södermann, and Tyrén has been carefully analyzed to arrive at a weighted average and an estimated probable error from interconsistency. R. T. Birge in his 1945 paper essentially agrees with Bearden's earlier results. We adopt Birge's

1945 value,

$$N = (6.02338 \pm 0.00043) \times 10^{23} \text{ mol}^{-1} \quad (\text{chemical scale}).$$

#### E. The Velocity of Light, $c$

The discussion of all observations of this important constant by R. T. Birge in his 1941 paper is so complete and satisfactory that we see no reason for re-examination. Since 1941 a new, very precise and beautiful method of measurement has been devised by W. W. Hansen of Stanford utilizing cavity resonance of short radiowaves. The method promises to yield better precision than any heretofore. Preliminary results of this method indicate that no change in this constant within the order of accuracy assigned by Birge in 1941 is likely. Therefore, we adopt Birge's 1941 value, namely,

$$c = 299776 \pm 4 \text{ km/sec.}$$

#### F. Ratio, $r$ , of Chemical to Physical Scales of Atomic Weights

For this we adopt, in accord with Birge's 1941 estimate,

$$r = 1.000272 \pm 0.000005.$$

#### G. The Electronic Charge $e$ (Computed as a Primary Datum, Old Viewpoint)

The quotient  $F/N$ , if each of these constants were known with certainty, would give the electronic charge  $e$ . Following what we call here the old viewpoint, this is treated as a primary datum, the three unknowns being regarded as  $e$ ,  $m$ , and  $h$ . For purposes of comparison only, in order to make as complete a least squares adjustment as the old viewpoint permits, we must choose an input value of  $e$  and for this purpose *and this purpose only* we adopt

$$e = F/N = (1.60184 \pm 0.00033) \times 10^{-20} \text{ e.m.u.}$$

or

$$= (4.80193 \pm 0.00100) \times 10^{-10} \text{ e.s.u.}$$

Since this is an input datum it cannot be expected to agree exactly with the final adjusted best value even on the old viewpoint method of adjustment and even less can it be expected to agree with the adjusted best value under the

<sup>21</sup> J. W. M. DuMond and V. L. Bollman, Phys. Rev. **50**, 524 (1936); V. L. Bollman and J. W. M. DuMond, Phys. Rev. **54**, 1005 (1938); P. H. Miller, Jr. and J. W. M. DuMond, Phys. Rev. **57**, 198 (1940).

<sup>22</sup> J. A. Bearden, J. App. Phys. **12**, 395 (1941); R. T. Birge, Am. J. Phys. **13**, 63 (1945).



TABLE III. Values of  $e/m$ .

$e/m$	Probable error	Weight	Author	Method	Date
1.75704	$7.0 \times 10^{-4}$	2	Kinsler and Houston	Zeeman effect	1934
1.76111	$10.0 \times 10^{-4}$	1	Perry and Chaffee	Direct velocity	1930
1.75901	$9.0 \times 10^{-4}$	1	Kirchner	Direct velocity	1931, 1932
1.75986	$4.0 \times 10^{-4}$	6	Dunnington	Mag. deflection	1933, 1937
1.75827	$13.0 \times 10^{-4}$	0.6	Shaw	Crossed fields	1938
1.75877	$8.0 \times 10^{-4}$	2	Goedicke	Busch method	1939

new viewpoint which latter is the value we recommend for adoption.

#### H. Specific Charge of the Electron, $e/m$ (Computed as a Primary Datum, Old Viewpoint)

Under the old viewpoint three distinctly different sources of information, as already explained, have usually been combined in order to find an input value of  $e/m$ . This premature scrambling of different experiments which in reality determine  $e/m$ ,  $F(e/m)$ , and  $(e/m)/F$  before making a least squares adjustment we believe to be incorrect. As in the case of  $e$  then, for the old viewpoint only, we adopt as an input datum

$$e/m = (1.75903 \pm 0.00050) \times 10^7 \text{ abs. e.m.u. g}^{-1}.$$

We have obtained this value and its probable error from a recalculation of R. T. Birge's 1941 data.<sup>23</sup> The recalculation has involved only very minor changes consistent with our present adopted input values of  $F$ ,  $p$ , and  $q$ .

#### I. Specific Charge of the Electron, $e/m$ (Input Datum, New Viewpoint)

On the new viewpoint in which  $F$ ,  $N$ , and  $h$  are regarded as unknowns (after elimination of  $m$  by the Rydberg relation) only two types of experiment lead directly to  $e/m$ , namely, the so-called deflection experiments and the Zeeman effect. From the table of Birge referred to in the previous paragraph<sup>23</sup> we have taken therefore the six values numbered 6, 8, 9, 10, 11, 12. These have been corrected for the slight revisions in  $p$  and  $q$  and weighted inversely as the squares of the stated probable errors with the results shown in Table III. In this way we receive for our

<sup>23</sup> See Table II of "The general physical constants as of August 1941," p. 120, which clearly indicates in its last column how  $F$ ,  $p$ , and  $q$  have entered to obtain  $e/m$ .

TABLE IV. Atomic weight of the electron.

$mN$ (physical scale)	Relative probable error	Weight	Author	Method	Date
$\times 10^{-4}$			Drinkwater, Richardson, and W. E. Williams	$H_\alpha$ and $D_\alpha$	1940
5.48650	$1.85 \times 10^{-4}$	3.0	Houston; Chu	$R_H$ and $R_{He}$	1927, 1939
5.48226	$3.13 \times 10^{-4}$	1.0	R. C. Williams	$H_\alpha$ and $D_\alpha$	1938
5.49009	$2.66 \times 10^{-4}$	1.4	C. F. Robinson	$H_\alpha$ and $D_\alpha$	1939
5.48643	$2.66 \times 10^{-4}$	1.4	Shane and Spedding	$H_\alpha$ and $D_\alpha$	1935
5.48951	$3.25 \times 10^{-4}$	0.8			

input datum on  $e/m$

$$e/m = F/(Nm) = (1.75920 \pm 0.00038) \times 10^7 \text{ abs. e.m.u. g}^{-1}.$$

#### J. Atomic Weight of the Electron, $mN$ , by Spectroscopy

On the new viewpoint the comparison of the wave-lengths of the  $H_\alpha$  and  $D_\alpha$  lines and of  $R_H$  and  $R_{He}$  give  $mN$ . These values have been recomputed from the original data given by Birge<sup>24</sup> with the results shown in Table IV.  $F$  is not involved in this computation.

In this way we receive for our input data on  $mN$  (the atomic weight of the electron) the mean values:

$$mN = (5.48690 \pm 0.00075) \times 10^{-4} \text{ (physical scale)} \\ = (5.48541 \pm 0.00075) \times 10^{-4} \text{ (chemical scale).}$$

#### K. Bearden's Determination of the X-Ray Refractive Index of Diamond

This experiment, usually classified (old viewpoint) as a determination of  $e/m$ , actually gives  $F^2/(Nm)$ . We receive for this input datum

$$F^2/(Nm) = F(e/m) = (1.69824 \pm 0.00035) \times 10^{11} \text{ e.m.u. (chemical scale).}$$

#### L. Evaluation of $h/e$ from Measurements of the Quantum Limit of the Continuous X-Ray Spectrum

This is the only datum used in the present paper which has undergone recent experimental revaluation and it will therefore now be discussed in somewhat more detail than the rest. The two recent redeterminations are those of Panofsky, Green, and DuMond in Pasadena

<sup>24</sup> R. T. Birge, "Values of  $R$  and of  $e/m$ ," Phys. Rev. 60, 766 (1941).

and P. Ohlin in Uppsala.<sup>25</sup> The experiment consists essentially in applying a very constant accurately measured high potential, accurately adjustable in very small steps to an x-ray tube, and observing the intensity of the continuous x-ray spectrum at a sharply defined accurately measured wave-length selected by means of a crystal monochromator. The curves of intensity *versus* voltage taken with a fixed monochromator setting are called isochromats. Only a small voltage range need be explored on either side of the threshold value, a small fraction of one percent of the threshold value being ample. The shape of the continuous spectrum from a thick target is essentially unmodified for such small changes. The entire pattern is merely displaced toward higher frequencies linearly with increasing voltage. Hence, the shape of the observed isochromat plotted against applied voltage becomes a mirror image of the shape of the continuous spectrum plotted against frequency save for the slight blurring effects chiefly ascribable to the finite resolving power of the monochromator ("window curve").<sup>26</sup> If  $\lambda_m$  is the wave-length setting of the monochromator and  $V_c$  the critical voltage on the isochromat corresponding to the threshold for the continuous spectrum, then aside from small corrections we have

$$eV_c = h\nu = hc/\lambda_m,$$

so that

$$h/e = V_c \lambda_m / c. \quad (10)$$

If Eq. (10) is to be regarded as rigorous then it is the belief of the present authors that to the measured voltage on the x-ray tube terminals<sup>27</sup> must be added the work function of the cathode of the x-ray tube to obtain the correct value of  $V_c$ .<sup>28</sup>

<sup>25</sup> W. K. H. Panofsky, A. E. S. Green, and J. W. M. DuMond, Phys. Rev. **62**, 214 (1942). P. Ohlin, Inaugural Dissertation, Uppsala (1941); Arkiv. f. Mat. Astro. och Fysik **27B**, No. 10; **29A**, No. 3; **29B**, No. 4; **31A**, No. 9; **33A**, No. 23.

<sup>26</sup> For discussions of the effect of the window curve and methods of determining the true threshold voltage from the isochromats see J. W. M. DuMond and V. L. Bollman, Phys. Rev. **51**, 413-423 (1937); W. K. H. Panofsky, A. E. S. Green, and J. W. M. DuMond, Phys. Rev. **62**, 215-216 (1942).

<sup>27</sup> Measured by means of a resistance divider conductively connected across the terminals of the tube, a calibrated fraction of the total P. D. being compared with a standard cell by potentiometer methods.

<sup>28</sup> For a discussion of the correction for cathode work function see J. W. M. DuMond and V. L. Bollman, Phys.

The work of P. Ohlin was done at much longer wave-lengths and therefore lower voltages than the work of Panofsky, Green, and DuMond, the former being in the region of 3 to 5 kv while the latter was at about 20 kv. The work function correction (of the order of 4 volts) is therefore a much more significant factor in Ohlin's case than in the high voltage work. Ohlin, however, in a beautiful series of experiments, has obtained internal experimental evidence which he interprets as unfavorable to making the work function correction. This is in such serious disaccord with theory and yet is such an essential point in correcting Ohlin's results that it is worth discussing here at some length.

In order to make all the relationships graphically clear we show in Fig. 6 the history of the values obtained for  $h/e$  by various experimenters over a long period of years. Two scales are shown, one for the values after making the cathode work function correction, the other when this correction is not made. Our final adjusted least squares best value for  $h/e$  is also plotted on this scale. It will be noted that most

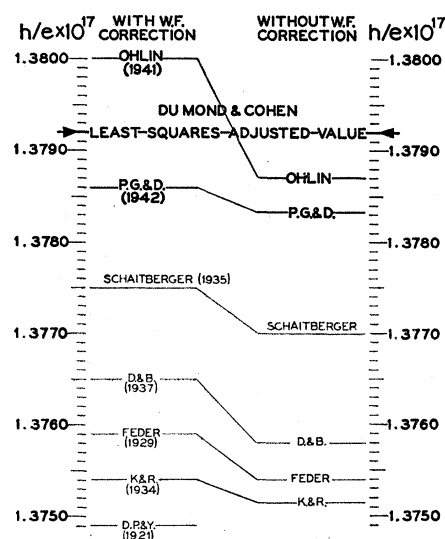


FIG. 6. Graph of different observed values of  $h/e$  from the quantum limit of the continuous x-ray spectrum over a period of twenty years. Only the values shown in heavy print are at present given consideration. The scale on the left gives the values when the correction for the cathode work function has been made. Those on the right give the values without this correction.

Rev. **51**, 412-413 (1937) and W. K. H. Panofsky, A. E. S. Green, and J. W. M. DuMond, Phys. Rev. **62**, 224 (1942).

of the older values are much too low. The reason for most of these is now well understood. A "knee" in the structure of the isochromats within ten or fifteen volts of the threshold, which because of lower spectral resolving power in the earlier work was not known to exist, was discovered when the two-crystal spectrometer was applied to this problem by DuMond and Bollman.<sup>29</sup> The earlier workers extrapolated their isochromats to find the quantum threshold but since they ignored the knee, their extrapolated voltages were too low. However, the absolute value of  $h/e$  obtained by DuMond and Bollman was itself too low because of thermal effects in the resistance divider discovered later and mentioned by Panofsky, Green, and DuMond. We believe it is now safe to ignore all the direct experimental results in Fig. 6 save those of Ohlin and P., G., and D. It will be noted that these results agree with each other somewhat better if the work function correction is not applied but their mean agrees better with our least squares adjusted value of  $h/e$  if this correction is applied.

Ohlin's internal evidence against applying the work function correction consisted principally in comparing the results he obtained for  $h/e$  at a number of different voltages (and wave-lengths).

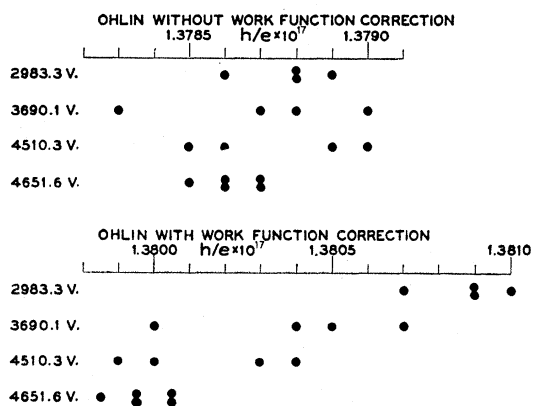


FIG. 7. Ohlin's individual observed values of  $h/e$  made at different voltages and monochromatizing wave-lengths both with and without correction for the work function. The voltages (quantum limit) of the different sets of results are shown. The corresponding monochromatizing wave-lengths were (in order of increasing voltage) those of  $\text{AgL}\alpha_1$ ,  $\text{CaK}\alpha_1$ ,  $\text{TiK}\alpha_1$  and  $\text{VaK}\alpha_1$ . It will be noted that the results are more consistent if the work function correction is not made.

These seemed to agree better when the constant additive work function correction was omitted. Unfortunately, the dispersion of his measurements is large enough so that the conclusion is not extremely clear cut. In Fig. 7 we graph Ohlin's individual results at different voltages on a very open scale of  $h/e$ , both with and without the correction. Their consistency seems better in the latter case.

Ohlin, who visited this country recently, has discussed his results with one of us and he frankly admits that he cannot see any escape from the logic of making the work function correction other than to suppose that some other unknown compensating effect exists. Prior to his visit a possible explanation of this sort was presumed by one of us to exist in the form of very thin deposits, probably consisting of hydrocarbons or other low atomic number materials, on Ohlin's target. It has been shown by Panofsky, Green, and DuMond<sup>30</sup> that such deposits (which are very hard to avoid in continuously pumped apparatus unless the target is continually cleaned mechanically during the course of the observations) can readily shift the apparent position of the isochromat threshold by many volts. This shift is ascribed to electron retardation in the hydrocarbon film which, because of its low atomic number, emits negligible continuous spectral intensity. By presuming the existence of a layer of carbon only one micron thick on Ohlin's target and correcting his results for the different retardations in this layer at his different voltages, the entire situation illustrated in Fig. 7 would be completely reversed as shown in Fig. 8. The data would then not only be more internally consistent if the work function correction were applied but the value of  $h/e$  would agree better with the P., G., and D. results and with the least squares adjusted mean value of this constant. *However, Ohlin assures us that careful examination of his targets failed to reveal any evidence of such carbon layers even after long continued operation.* A one-micron layer should have been easy to see. We must, therefore, abandon this explanation. We show Fig. 8 merely to illustrate how a small systematic

<sup>29</sup> See  $K_3$  in Fig. 14 of J. W. M. DuMond and V. L. Bollman, Phys. Rev. **51**, 416 (1937).

<sup>30</sup> W. K. H. Panofsky, A. E. S. Green, and J. W. M. DuMond, Phys. Rev. **62**, 217-218 (1942). See especially Fig. 2.

source of error of this kind could affect Ohlin's conclusions regarding the invalidity of the work function correction. We are unable to see any plausible reason for such a systematic error however.

Ohlin has also tried comparing the values of  $h/e$  he obtains using, on the one hand, an uncoated tungsten cathode and, on the other hand, a BaO-coated platinum cathode.<sup>31</sup> Here again the uncorrected value of  $h/e$  seemed to be independent of the nature of the cathode. The work function of the coated cathode was presumably much lower than that of the tungsten. Unfortunately, in no case has Ohlin actually measured the work functions of the cathodes he used. Now it is a well-known fact that thermionic cathode work functions can vary widely (and either upward or downward) from the influence of very slight contaminations on their surfaces. In view of the theoretical and practical importance of his results we have urged him to repeat the experiments with provision for measuring his cathode work function. This can be done with sufficient precision for the purpose at hand by providing means of observing the cathode temperature and measuring the heating power which must be supplied to keep the cathode at constant temperature as a function of the emission current drawn off at different applied voltages.

On the theoretical side the absence of the necessity for any cathode work function correction is very difficult to understand. There can be no doubt that the method of measuring the P.D. between the cathode and target of the tube with a resistance potential divider actually measures the energy level difference (in volts) between the uppermost filled electron levels in target and cathode terminals. Errors from ther-

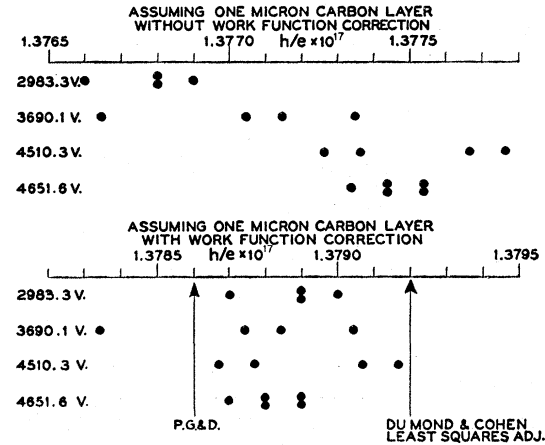


FIG. 8. Ohlin's individual observed values of  $h/e$  corrected for the existence of a hypothetical retarding layer of carbon deposit one micron thick on the target. Here the results are more internally consistent if the work function correction is applied and also agree better with the  $h/e$  value of Panofsky, Green, and DuMond and with the least squares adjusted value of  $h/e$  from all sources. Ohlin is certain from inspection that no such deposits existed on his target, and the plot is merely shown here to illustrate how small a systematic error of this sort could reverse his conclusions regarding the inapplicability of the work function correction.

mal e.m.f.'s, Kelvin P.D.'s, etc. are far too small to be significant. Relative to the uppermost filled levels in the target the electrons emitted from the cathode have received energy  $eV$  from the high potential source and energy  $e\phi$  from the thermal energy supplied to heat the cathode where  $V$  is the measured voltage and  $\phi$  the cathode work function. The maximum amount of energy available to convert into x-rays is therefore  $eV + e\phi = h\nu_{\max}$ , corresponding to transitions of cathode ray electrons to the lowest unfilled final state in the target at the top of the partially filled Fermi band. It would seem that this energy state for electrons would exist with-

TABLE V. Values of constants on which computations are based (old viewpoint).

Inserted value	Origin value	Relative difference	Probable error
1 $R_{\infty}=109737.3$	$R_{\infty}=109737.08$	$a_1=0.000002$	0.00
2 $e=4.80193$	$e_0=4.80650$	$a_2=-0.000953$	$1.24 \times 10^{-4}$
3 $e/m=1.75903$	$e_0/m_0=1.75850$	$a_3=0.000302$	$2.8 \times 10^{-4}$
4 $h/e=1.37860$	$h_0/e_0=1.38028$	$a_4=-0.00122$	$2.9 \times 10^{-4}$
5 $h/(em)^{1/2}=1.00084$	$h_0/(e_0m_0)^{1/2}=1.002157$	$a_5=-0.00132$	$5.8 \times 10^{-4}$
6 $e^2/(mh)=3.8197$	$e_0^2/(m_0h_0)=3.81920$	$a_6=0.000131$	$10.5 \times 10^{-4}$
7 $\alpha=7.30194 \times 10^{-3}$	$\alpha_0=7.29870 \times 10^{-3}$	$a_7=0.00044$	$3.7 \times 10^{-4}$
8 $h/m=7.267$ (Gnan)	$h_0/m_0=7.27621$	$a_8=-0.00127$	$12.4 \times 10^{-4}$
8c $h/m=7.255$ (R. and K.)	$h_0/m_0=7.27621$	$a_{8c}=-0.00292$	$30.3 \times 10^{-4}$

<sup>31</sup> P. Ohlin, Arkiv. f. Math. Astro. och Fysik **29B**, No. 4.

TABLE VI. Old viewpoint. Adjusted values of the atomic constants and other derived constants. (Not recommended but given only for purposes of comparison.)

$e = (4.8021 \pm 0.0005) \times 10^{-10}$ abs. e.s.u.
$m = (9.1055 \pm 0.0020) \times 10^{-28}$ g
$h = (6.6233 \pm 0.0011) \times 10^{-27}$ erg sec.
$F = 9648.2 \pm 1.0$ e.m.u. equiv. <sup>-1</sup>
$N = (6.0229 \pm 0.0004) \times 10^{23}$ mol <sup>-1</sup>
$e/m = (1.75927 \pm 0.00035) \times 10^7$ e.m.u. g <sup>-1</sup>
$h/e = (1.37924 \pm 0.00013) \times 10^{-17}$ erg sec. e.s.u. <sup>-1</sup>
$\alpha = (137.030 \pm 0.011)^{-1}$
$\lambda_c = (2.42645 \pm 0.00038) \times 10^{-10}$ cm

out modification within a very few atom diameters of the target surface, and it is very difficult indeed to see any mechanism that can forbid transitions of the impinging cathode rays to this state. Such transitions will surely result in the frequency  $\nu_{\max}$  at the quantum limit of the continuous spectrum. It has been argued that perhaps the transitions occur *at the target surface or even just outside it* and that the final state of the electron is therefore that of a free electron at the surface of the target. This electron by further transitions then eventually reaches the levels of the conduction band inside the target. In such a case the equation of energy conversion would become  $eV + e\varphi_c - e\varphi_t = h\nu_{\max}$  and since  $\varphi_c$  and  $\varphi_t$ , the work functions of cathode and target, respectively, are of the same order of magnitude, the net correction would be negligible. The second subsequent transition to the top of the Fermi sea would result in radiation too soft to be observed. Doubtless just such multiple transitions *do* occur but it still remains unexplained *why single transitions to the lowest internal states are forbidden*.

There seems to be evidence in Ohlin's own isochromats that the final state of the electron is

one of the permitted *internal* energy states or bands of the target lattice. The arguments leading to this conclusion have been presented recently by DuMond.<sup>32</sup> If this is correct, it is very difficult to see how the lowest of these unfilled internal states could be forbidden as a final state for the impinging cathode ray electrons.

These difficulties and uncertainties regarding the work function correction, which in Ohlin's work, because of his low voltages, would make a large relative change in his numerical value of  $h/e$ , have obliged us to omit using his results at the present time. We have, therefore, based our input value of  $h/e$  entirely on the P., G., and D. results *corrected for the work function of the tantalum cathode (4 volts or relatively only 2 parts in  $10^4$ )*. We have made a numerical test which shows that our final adjusted values of the constants are insignificantly affected by a change of the order of this work function in our case. We have increased the estimated probable error of the P., G., and D. results from  $\pm 0.0002$  to  $\pm 0.0004$  because of the uncertainty regarding the *value* of the work function which, as we have pointed out above, might have been considerably increased or decreased by surface contaminations. We thus arrive at the following input value:

$$h/e = hN/F = (1.3786 \pm 0.0004) \times 10^{-17} \text{ erg sec. e.s.u.}^{-1}.$$

#### M. $h/(em)^{1/2}$ from Von Friesen's Electron Diffraction Experiments

For this constant we have used, without modification, the value recomputed earlier by

TABLE VII. Input values, new viewpoint.

	Source
1. $N = (6.02338 \pm 0.00043) \times 10^{23}$ (chemical scale)	X-ray crystal method
2. $F = 9648.5 \pm 1.0$ abs. e.m.u. equiv. <sup>-1</sup> (chemical scale)	I and Ag voltameters
3. $mN = (R_\infty/2\pi^2c^3)F^{-1}N^5h^3 = (5.48541 \pm 0.00075) \times 10^{-4}$ (chemical scale)	Spectroscopic fine structure
4. $F(e/m) = (2\pi^2c^3/R_\infty)F^6N^{-5}h^{-3} = (1.69824 \pm 0.00035) \times 10^{11}$ (chemical scale)	X-ray refractive index of diamond
5. $e/m = (2\pi^2c^3/R_\infty)F^6N^{-5}h^{-3} = (1.75920 \pm 0.00038) \times 10^7$ e.m.u. g <sup>-1</sup>	Deflection methods; Zeeman effect
6. $h/e = chN/F = 1.3786 \pm 0.0004$ erg sec. e.s.u. <sup>-1</sup>	Continuous x-ray spectrum
7. $\alpha = 2\pi cF^2N^{-2}h^{-1} = (136.95 \pm 0.05)^{-1}$	X-ray doublets (Christy and Keller)
8. $h/(em)^{1/2} = (2\pi^2c^2/R_\infty)^{1/2}h^{-1}F^{1/2}N^{-1/2} = (1.00084 \pm 0.00058) \times 10^{-8}$ e.s.u.	Von Friesen experiment
9. $h/m = (2\pi^2c^2/R_\infty)F^4N^{-4}h^{-2} = 7.267 \pm 0.009$ c.g.s. unit	Gnan experiment
10. $e^2/mh = (2\pi^2c^5/R_\infty)F^6N^{-6}h^{-4} = (3.8197 \pm 0.0045) \times 10^{34}$ e.s.u.	Robinson and co-workers

<sup>32</sup> J. W. M. DuMond, Phys. Rev. **72**, 276 (1947).

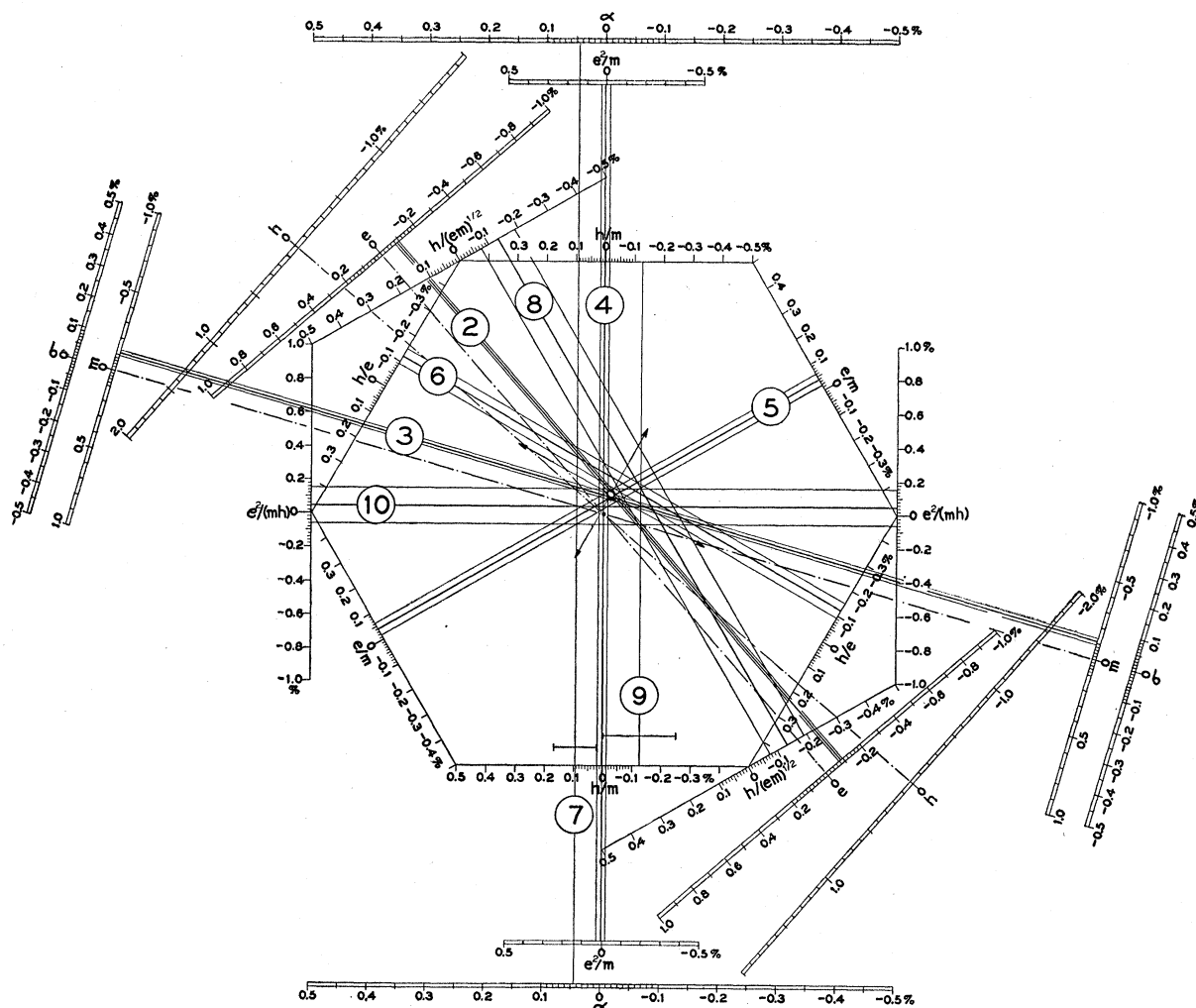


FIG. 9. Isometric consistency chart under the new viewpoint showing the input data and their probable errors by the full lines. The plot is made assuming Avogadro's number at the least squares adjusted best value. The origin values for the chart are given in Section III-A. The numbered input data correspond to the following experiments: 2. Faraday constant (average of Ag and I voltameters). 3. Atomic mass of electron by spectroscopy ( $H_\alpha$  and  $D_\alpha$ ;  $R_H$  and  $R_{H\alpha}$ ). 4.  $e^2/m$  from Bearden's measurement of the x-ray refractive index of diamond. 5.  $e/m$  by direct deflection methods. 6.  $h/e$  Panofsky, Green, and DuMond, continuous x-ray limit. 7. Christy and Keller's evaluation of  $\alpha$ . 8. Von Friesen's  $h/(em)^{1/2}$ . 9. Gnan's  $h/m$ . 10. Robinson and co-workers  $e^2/(mh)$ . The center of the small white ellipse of probable error gives our recommended least squares adjusted best value. The axes of this ellipse are indicated with arrows. This cut has not been revised to accord with certain small corrections to our numerical values found necessary after the paper had been submitted. Such changes are wholly unimportant.

F. G. Dunnington<sup>33</sup> for our input value, namely:

$$h/(em)^{1/2} = (1.00084 \pm 0.00058) \times 10^{-8} \text{ e.s.u.}$$

#### N. $e^2/(mh)$ Obtained from Magnetic Deflection of X-Ray Photoelectrons Ejected by Radiation of Known Quantum Energies

This experiment was carried out by two independent workers, H. R. Robinson<sup>34</sup> and co-

workers on the one hand and G. G. Kretschmar on the other hand.<sup>35</sup> Kretschmar's work is subject to systematic errors of amount difficult to evaluate as Dunnington<sup>36</sup> has pointed out. From Robinson and his co-workers we adopt as our

<sup>34</sup> H. R. Robinson, *Phil. Mag.* **22**, 1129 (1936); H. R. Robinson and C. J. B. Clews, *Proc. Roy. Soc.* **A176**, 28 (1940); R. L. Mayo and H. R. Robinson, *Proc. Roy. Soc.* **A173**, 192 (1939).

<sup>35</sup> G. G. Kretschmar, *Phys. Rev.* **43**, 417 (1933).

<sup>36</sup> F. G. Dunnington, *Rev. Mod. Phys.* **11**, 70 (1939).

<sup>33</sup> F. G. Dunnington, *Rev. Mod. Phys.* **11**, 68 (1939).

input value,

$$e^2/(mh) = (3.8197 \pm 0.0045) \times 10^{34} \text{ e.s.u.}$$

#### O. Determination of the Fine Structure Constant $\alpha$

The input value for this constant has been taken from the work of Christy and Keller<sup>37</sup> using R. T. Birge's<sup>38</sup> estimate of the probable error, namely,

$$\alpha = 2\pi e^2/(hc) = 1/(136.95 \pm 0.05).$$

#### P. $h/m$ by Electron Diffraction in Which the Electron Speeds are Measured Kinematically, Compton Shift Measurements of $h/(mc)$

These yield the least accurate data considered here. In fact, the Compton shift measurements have so large an uncertainty and, hence, are weighted so lightly that they have been dropped from consideration in the calculations under the new viewpoint. For the electron diffraction results on  $h/m$  we have taken Gnan's value as re-

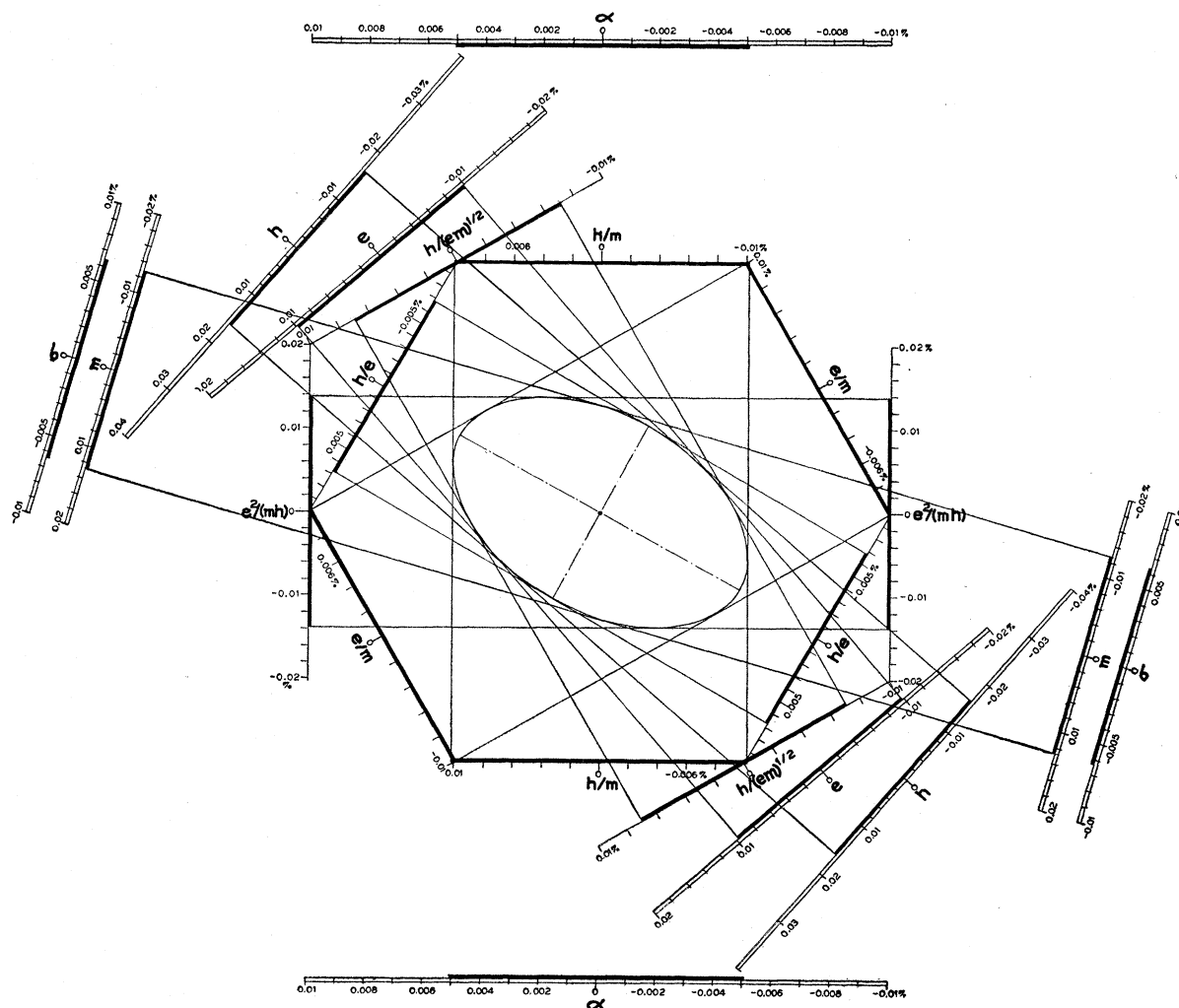


FIG. 10. Ellipse of probable error to large scale for the recommended least squares adjusted best values of the constants (new viewpoint).

<sup>37</sup> R. F. Christy and J. M. Keller, Phys. Rev. 58, 658 (1940).

<sup>38</sup> R. T. Birge, Phys. Rev. 58, 658 (1940).

computed by F. Kirchner in his 1939 review<sup>39</sup> of the atomic constants. This gives us the input value

$$(h/m)_{\text{Gnan}} = 7.267 \pm 0.009 \text{ c.g.s. units.}$$

The measurements of Compton shift by Ross and Kirkpatrick have been carefully reviewed and recomputed by F. Kirchner<sup>39</sup> and we have used his value which, upon multiplication by  $c$ , gives for our input value

$$(h/m)_{\text{R and K}} = 7.255 \pm 0.022 \text{ c.g.s. units.}$$

This completes the consideration of our primary sources of data.

### III. LEAST SQUARES ADJUSTMENTS OF THE DATA

#### A. The Origin Values

The origin values  $e_0$ ,  $m_0$ ,  $h_0$  and functions thereof are quite arbitrarily chosen save that, for convenience, they have been made closely consistent with the Rydberg relation and our adopted value of that constant. They have purposely been chosen sufficiently different from the expected best adjusted values so that the origin point and the  $e$ ,  $m$ ,  $h$  axes on our charts will not be confused with the other intersections. Our origin values given below have been used both for plotting our charts<sup>40</sup> and for the computations in the least squares adjustments.

$$e_0 = 4.80650 \times 10^{-10}; \quad m_0 = 9.11780 \times 10^{-28}; \\ h_0 = 6.63430 \times 10^{-27}$$

Using  $c = 2.9977600 \times 10^{10}$  these values yield  $R_\infty = 109737.08$  which is in error by only 2 parts in  $10^6$ . Also consistent with  $e_0$  we take, for the purpose of calculations under the new viewpoint, the origin values

$$N_0 = 6.020000 \times 10^{23} \quad \text{and} \quad F_0 = 9652.250.$$

(We shall use the chemical scale throughout our calculations.)

<sup>39</sup> F. Kirchner, "Die Atomaren Konstanten," *Ergebnisse der Exakten Naturwiss.* 18, 66 (1939). We have given preference to Kirchner's value because of his intimate knowledge of this work.

<sup>40</sup> Except for the charts of Figs. 2 and 10 which have the "best" or "least squares" values at the origin.

#### B. Least Squares Adjustment under the Old Viewpoint

Under the old viewpoint the unknowns are  $e$ ,  $m$ , and  $h$ . Table V gives the numerical values on which the computations are based. The  $a$ 's in the third column are the relative differences (such as  $(e - e_0)/e_0$ ) between each quantity and its origin value.

From these data nine linear equations in  $x_e$ ,  $x_m$ , and  $x_h$  are written and  $x_m$  is eliminated by means of the Rydberg relation. We thus obtain the eight observational equations which we have weighted as shown:

	Weight
$x_e = -9.53$	65 (2)
$5x_e - 3x_h = 3.02$	13 (3)
$-x_e + x_h = -12.2$	12 (4)
$\frac{3}{2}x_e - \frac{1}{2}x_h = -13.2$	3 (5)
$6x_e - 4x_h = 1.3$	0.9 (6)
$2x_e - x_h = 4.4$	7.3 (7)
$4x_e - 2x_h = -12.7$	0.7 (8)
$4x_e - 2x_h = -29.2$	0.1 (8c)

For convenience, the variables have been defined as

$$x_e = (e - e_0)/e_0 \times 10^4; \quad x_m = (m - m_0)/m_0 \times 10^4; \\ x_h = (h - h_0)/h_0 \times 10^4.$$

A least squares adjustment of these observational equations leads to the following results for the adjusted output values and their probable errors (old viewpoint method).

#### C. Least Squares Adjustment under the New Viewpoint

The unknown variables are  $F$ ,  $N$ ,  $m$ , and  $h$ . The data usually classified as leading to  $e/m$  now fall in three distinct categories. There are now eleven observational equations, one of which, the Rydberg relationship, is regarded as exact. By means of this equation the variable  $m$  is eliminated, leading to a set of ten observational equations in three variables  $F$ ,  $N$ , and  $h$ . Adopting the origin values given above this method leads to the input values of Table VII and to the following observational equations with their probable errors and weights. (The numbering is, of course, different from that of the old viewpoint.)



TABLE VIII. Least square fitted values of the atomic constants. (Recommended values, 1947.)

$F$	Faraday	$9649.6 \pm 0.7$ e.m.u. equiv. <sup>-1</sup> (chemical scale)
$N$	Avogadro's number	$9652.2 \pm 0.7$ e.m.u. equiv. <sup>-1</sup> (physical scale)
		$(6.0235 \pm 0.0004) \times 10^{23}$ (chemical)
		$(6.0251 \pm 0.0004) \times 10^{23}$ (physical)
$h$	Planck's constant	$(6.6234 \pm 0.0011) \times 10^{-27}$ erg sec.
$m$	Electron mass	$(9.1055 \pm 0.0012) \times 10^{-28}$ g
$e$	Electronic charge	$(4.8024 \pm 0.0005) \times 10^{-10}$ e.s.u.
		$(1.60199 \pm 0.00016) \times 10^{-20}$ e.m.u.
$h/e$		$(1.37920 \pm 0.00009) \times 10^{-17}$ erg sec. e.s.u. <sup>-1</sup>
$e/m$	Specific electronic charge	$(1.75936 \pm 0.00018) \times 10^7$ e.m.u. g <sup>-1</sup>
		$(5.2741 \pm 0.0005) \times 10^{17}$ e.s.u. g <sup>-1</sup>
$h/m$		$(7.2741 \pm 0.0007)$ cm <sup>2</sup> sec. <sup>-1</sup>
$\alpha$	Fine structure constant	$(7.2981 \pm 0.0004) \times 10^{-3}$
$\alpha^2$		$(5.3263 \pm 0.0005) \times 10^{-5}$
$1/\alpha$		137.021 $\pm$ 0.007
$h/mc$	Compton wave-length	$(2.42650 \pm 0.00025) \times 10^{-10}$ cm
$\frac{1}{4\pi c} e/m$	Zeeman displacement per gauss	$(4.6703 \pm 0.0005)$ cm <sup>-1</sup> gauss <sup>-1</sup>
$a_0 = h^2/(4\pi^2 me^2)$	"First Bohr radius"	$(0.529161 \pm 0.000028) \times 10^{-8}$ cm
$a_0' = a_0(1 - \alpha^2)^{1/2}$	Separation of electron and proton in the ground state of H <sup>1</sup>	$(0.529147 \pm 0.000028) \times 10^{-8}$ cm
$a_0'' = a_0' R_\infty / R_H$	Radius of the electron orbit, referred to center of mass, for normal H <sup>1</sup>	$(0.529435 \pm 0.000028) \times 10^{-8}$ cm
$\frac{1}{16} R_H \alpha^2$	Doublet separation in hydrogen	$(0.365110 \pm 0.000038)$ cm <sup>-1</sup>
$\sigma$	Stefan-Boltzmann constant	$(5.6724 \pm 0.0023) \times 10^{-5}$ erg cm <sup>-2</sup> deg. <sup>-4</sup> sec. <sup>-1</sup>
$c_1 = 8\pi hc$	First radiation constant	$(4.9902 \pm 0.0008) \times 10^{-16}$ erg cm
$c_2 = hc/k$	Second radiation constant	$(1.43847 \pm 0.00019)$ cm deg.
$\lambda_{max} T$	Wien displacement law constant	$(0.289715 \pm 0.000039)$ cm deg.
$\mu_1 = he/4\pi m$	Bohr magneton	$(0.92731 \pm 0.00017) \times 10^{-20}$ erg gauss <sup>-1</sup>
$(3k/N)^{1/2}$	Multiplier of (Curie constant) <sup>1/2</sup> to give magnetic moment per molecule	$(2.62196 \pm 0.00017) \times 10^{-20}$ (erg mol deg. <sup>-1</sup> ) <sup>1/2</sup>
$h/k$	Atomic specific heat constant = $c_2/c$	$(4.7985 \pm 0.0007) \times 10^{-11}$ sec. deg.
$\mu = mH^+/H$	Reduced mass of electron in the hydrogen atom	$(9.1006 \pm 0.0012) \times 10^{-28}$ g
$8\pi^2 m/h^2$	Schrödinger constant for fixed nucleus	$(1.63881 \pm 0.00039) \times 10^{27}$ erg <sup>-1</sup>
$8\pi^2 \mu/h^2$	Schrödinger constant for the hydrogen atom	$(1.63792 \pm 0.00039) \times 10^{27}$ erg <sup>-1</sup>
$mN$	Atomic weight of the electron	$(5.4847 \pm 0.0006) \times 10^{-4}$ (chemical)
		$(5.4862 \pm 0.0006) \times 10^{-4}$ (physical)

These input values, insofar as the two dimensional chart permits, are shown graphically in Fig. 9, and the consistency of the input data can be judged graphically from this. Observational equations are:

			$P.E.$	$\times 10^4$ Weights
1.	$x_N$	=	5.61	0.71 19.8
2.	$x_F$	=	-3.98	1.04 9.2
3.	$-4x_F + 5x_N + 3x_h$	=	-6.41	1.4 5.3
4.	$6x_F - 5x_N - 3x_h$	=	5.28	2.1 2.4
5.	$5x_F - 5x_N - 3x_h$	=	4.01	2.2 2.1
6.	$-x_F + x_N + x_h$	=	-12.15	2.9 1.2
7.	$2x_F - 2x_N - x_h$	=	4.43	3.7 0.8
8.	$\frac{3}{2}x_F - \frac{3}{2}x_N - \frac{1}{2}x_h$	=	-13.13	5.8 0.3
9.	$4x_F - 4x_N - 2x_h$	=	-12.64	12.4 0.1
10.	$6x_F - 6x_N - 4x_h$	=	1.32	10.5 0.1

The three normal equations formed from the above set by the standard procedure of least squares lead to the final adjusted best values with their probable errors given in Table VIII at the end of this article. These are the values which we recommend. The probable errors are computed from the minors of the normal determinant and from the constant terms of the normal equations. Figure 10 shows with the exception of  $(P.E.)_F$  and  $(P.E.)_N$  how these are related as projected widths of the error ellipse (marginal probable error). The probable errors reflect not only the estimated probable errors of the input data but also the interconsistency of the entire observational data. The comparison of external and internal consistency gives  $r(\text{external})/r(\text{internal}) = 1.0$ .

TABLE VIII.—Continued.

$H^+/mN$	Ratio, proton mass to electron mass	$1836.57 \pm 0.20$
$\lambda_0$	Wave-length associated with 1 ev	$(12394.2 \pm 0.9) \times 10^{-8}$ cm
$\nu_0$	Frequency associated with 1 ev = $10^9 e/hc$	$(2.41867 \pm 0.00017) \times 10^{14}$ sec. <sup>-1</sup>
$\bar{\nu}_0$	Wave number associated with 1 ev	$8068.2 \pm 0.6$ cm <sup>-1</sup>
$E_0 = e \cdot 10^8/c$	Energy associated with 1 ev	$(1.60199 \pm 0.00016) \times 10^{-12}$ erg
$h/e$	Potential associated with unit frequency	$(1.37920 \pm 0.00009) \times 10^{-17}$ e.s.u.
$E_1 = hc$	Energy associated with unit wave number	$(1.98555 \pm 0.00032) \times 10^{-16}$ erg
$v_0 = [2 \cdot 10^8(e/m)]^{1/2}$	Speed of 1 ev electron	$(5.93188 \pm 0.00030) \times 10^7$ cm sec. <sup>-1</sup>
	Conversion factor, atomic mass units to Mev	
	1 a.m.u. =	$(931.04 \pm 0.07)$ Mev
$mc^2$	Energy equivalent of electron mass	$(0.51079 \pm 0.00006)$ Mev
$(R_0/F)10^{-8}$	Energy associated with 1° K	$k = (0.86163 \pm 0.00008) \times 10^{-4}$ ev
	"Temperature" associated with 1 ev	$(11605.9 \pm 1.0)^\circ$ K
$n_0$	Loschmidt's number	$(2.68731 \pm 0.00019) \times 10^{19}$ cm <sup>-3</sup>
$k$	Boltzmann's constant	$(1.38032 \pm 0.00011) \times 10^{-16}$ erg deg. <sup>-1</sup>
$S_0$	Sackur-Tetrode constant	$S_0/R_0 = -5.57191 \pm 0.00037$ $S_0 = (-46.3269 \pm 0.0038) \times 10^7$ erg mol <sup>-1</sup> deg. <sup>-1</sup>
	Auxiliary constants used.	
$c$	Velocity of light	$(2.99776 \pm 0.00004) \times 10^{10}$ cm sec. <sup>-1</sup>
$R_\infty$	Rydberg constant for "infinite" mass	$109737.30 \pm 0.05$ cm <sup>-1</sup> = $13.601$ e.v.
	Atomic masses (physical scale)	H = $1.008131 \pm 0.000003$ D = $2.014725 \pm 0.000006$ He = $4.003860 \pm 0.000031$
$R_0$	Gas constant per mol	$(8.31436 \pm 0.00038) \times 10^7$ erg mol <sup>-1</sup> deg. <sup>-1</sup>
$V_0$	Standard volume of perfect gas	$(22.4146 \pm 0.0006) \times 10^3$ cm <sup>3</sup> mol <sup>-1</sup>
	Conversion factors, NBS International units to absolute electrical units	
	1 NBS ohm = $p$ absolute ohm	$p = 1.000495$
	1 NBS volt = $pq$ absolute volts	$pq = 1.000330$
	1 NBS ampere = $q$ absolute ampere	$q = 0.999835$
$\lambda_g/\lambda_s$	Ratio, grating to Siegbahn scales of wave-length	$1.002030 \pm 0.000020$
$d_{20}$	Grating space of calcite (20°C)	$(3.03567 \pm 0.00005) \times 10^{-8}$ cm
$\rho$	Density of calcite (20°C)	$(2.71030 \pm 0.00003)$ g cm <sup>-3</sup>

#### D. Discussion of the Adjusted Best Values

Undoubtedly the most striking difference between the present results and any heretofore is the higher value of  $F$ . It is notable and perhaps significant that the weighted least square adjustment of all our information indicates a value for  $F$  *very closely in agreement with the iodine voltameter results*. It was, of course, to be expected that the adjusted value would be higher than the input value. Birge already has computed<sup>41</sup> by a comparison of the fine structure data ( $H_\alpha$  and  $D_\alpha$  and  $R_H - R_{He}$ ) with the deflection measurements of  $e/m$  that exact agreement as to  $e/m$  from these two sources alone would require a value of  $F = 96535$  int. coulombs (chemical scale). This is much higher than either silver (96494) or iodine (96511) values but the method of computation from the spectroscopic and de-

flection data alone is also subject to much larger error. Our present method which is an effort to give *all* the data their appropriate weights allowing the necessary freedom of adjustment in  $F$ ,  $N$ ,  $m$ , and  $h$  simultaneously must be regarded as the most impartial and objective way of finding the best compromise. The fact that this results in the iodine value for  $F$  seems to make it a matter of great interest to re-examine carefully, in the light of our modern knowledge of isotopes as well as all other possible sources of error, the silver and iodine voltameter experiments.<sup>42</sup> The difference between the input value of  $F$  ( $9648.5 \pm 1.0$  abs. e.m.u. equiv.<sup>-1</sup> (chemical scale), the mean of the silver and iodine work) and the output or adjusted value of  $F$  is 0.88 times the probable error of that difference. This does not seem

<sup>41</sup> R. T. Birge, Phys. Rev. **60**, 785 (1941).

<sup>42</sup> Dr. W. Vinal of the National Bureau of Standards has informed us that such a re-examination is now in progress there.

serious and we feel no hesitancy in recommending our value for adoption since it results in better agreement with all our sources of information than any other.

It will be noted that the adjusted value of  $N$  has changed very little indeed from our input value or from the values recommended in the past. This should be a source of considerable satisfaction to the workers (Bearden, Bäcklin, Södermann) who have devoted such care to this important constant with such eminently satisfactory results. There is a slight upward shift in  $e$  which is chiefly ascribable to the upward shift in  $F$  but the change is well inside the probable error of the difference between input or output values. The adjusted output value of  $h/e$  exceeds the Panofsky, Green, and DuMond (input) value by 1.5 times the probable error of this difference. This cannot be taken as proof of systematic errors in the measurement since such a deviation is not considered as excessive. The results of Ohlin's investigations as regards the work function correction should prove of great value. Should it develop that the work function must be added as a correction to his present results, then the average of Ohlin and P., G., and D. as to  $h/e$  will be in substantially better agreement with our present adjusted best value than P., G., and D. alone is now. If the work function correction is not made, however, the discrepancy from our best adjusted value will be serious.

In a very recent redetermination<sup>43</sup> at the Na-

<sup>43</sup> M. S. Van Dusen and A. I. Dahl, N.B.S. Research paper, RP 1828 from Bur. Stand. J. Research **39**, 291 (1947).

tional Bureau of Standards of the second radiation constant  $c_2$  by direct experimental means the mean result,  $c_2 = 1.438_2$  cm degrees has been obtained. (The three different individual results from which this mean is derived indicate by their consistency a probable error of  $\pm 0.0006$  in the above figure.) This agrees very well with (1) R. T. Birge's indirectly calculated 1941 value,  $c_2 = 1.43848 \pm 0.00034$  and (2) our present recommended value from our least squares adjustment,  $c_2 = 1.43847 \pm 0.00019$ . As Dr. Birge has pointed out in a recent letter to us, the International Temperature Scale has been and still is based on the value  $c_2 = 1.432$ , the same value as that recommended by him in 1929. Until the present work<sup>43</sup> there never had been an experimental value higher than  $c_2 = 1.436$  and this was one of the great discrepancies between directly observed and calculated values. This situation is, therefore, very much more satisfactory than ever before.

The chart, Fig. 9, shows that none of the input values of our data represented thereon deviate from our best adjusted output values seriously when each deviation is compared with the probable error spread of that input datum.

#### ACKNOWLEDGMENTS

The authors are much indebted to Professor R. T. Birge for pointing out the oversight, in their original manuscript, of his improved results regarding Avogadro's number which are published in his 1945 paper.<sup>1</sup> The numerical values in the present paper have been revised to accord with this result.